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The Structure and Stratigraphy of the North-West Indian Oilfield.

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Introduction.

The present paper is the outcome of some detailed mapping work, done in three widely separated areas of the above oilfield. This has elucidated certain features of stratigraphy and structure, which, it is hoped, will throw some light on the geological problems presented in the Salt Range, its trans-Indus extension, and the Kohat Hills.

These hills extend from the Jhelum River (lat. 32° 30′ long. E. 73° 30′) across the Indus River at Kalabagh to Sheikh Budin (lat. 32° 18′ long. E. 70° 45′) and as far north as Kohat (long. E. 71° 30′ lat. 33° 30′). Originally the Kohat Hills were regarded as the trans-Indus extension of the Salt Range, presumably because salt is common to both. It was not until about 1875, when Mr. A. B. Wynne of the Indian Geological Survey examined these ranges, that the Maidan and Khasor Ranges were realised to be the true trans-Indus Salt Range.

The position of these hills with reference to the Himalayan and Hindu Kush Systems is well shown by Diagram No. 1. Their average elevation is only between 2–3000 feet above sea-level, but a few peaks (*e.g.*, Sakesar, Sheikh Budin and Narai Sar) rise to about 4500 feet. The climate is very dry, and the majority of the streams are waterless except after rain. The waters of many of the smaller ones are salt. Rains are scarce, and chiefly confined to the higher altitudes. The temperature varies excessively between midday and midnight, and consequently erosion is severe. The vegetation is scanty, and very little soil is found, as a result the geological exposures are exceptionally good. Where the sequence is regular, it is often possible to map in the strata over wide areas, while standing on an eminence. The bright coloured assemblage of strata, comprising red, purple, green, yellow and white rocks, make up a most remarkable landscape.

Previous work done.—Owing to the unique occurrence in apparent conformity of rocks of all ages from supposed pre-Cambrian to late Tertiary, this has been one of the most discussed geological areas of the world, and a wealth of literature has appeared on the subject.

It would be impossible here to give even a summary of these papers. The more important ones are referred to in the text, and a bibliography is appended.

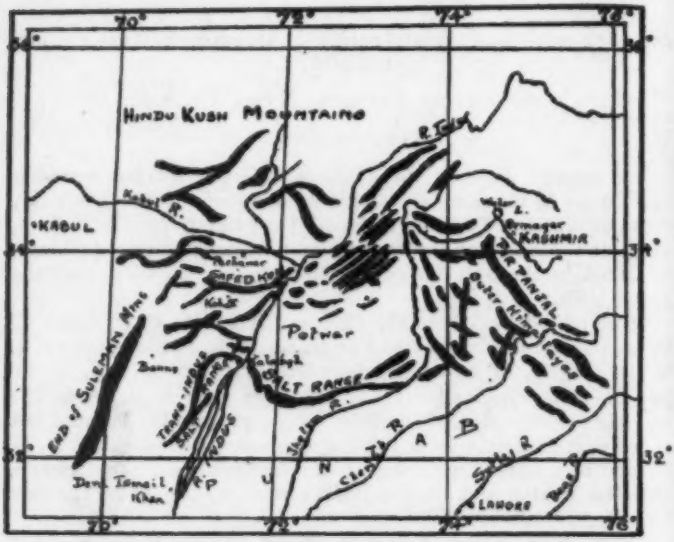


DIAGRAM 1.

SKETCH OF POSITION OF SALT RANGE, ETC.
(After Wynne, *Mem. G.S.I.*, Vol. 14, plate 8.

The most comprehensive work was done from 1875–1880 by Mr. Wynne.[1] In 1913 Dr. E. H. Pascoe, also of the Indian Geological Survey, studied the petroleum occurrences in this district and mapped many areas.[2] The earliest extensive attempt to classify the groups of strata outcropping was made by Dr. Fleming about 1850.[3] He correlated the rock groups closely with the European formations, placing the Red Marls and the Purple Sandstones in the Old Red Sandstone Series, and the Salt in the Trias. In 1853, however, he recognised the unsoundness of this classification.[4]

The following sequence, suggested by Wynne, has long been generally accepted, though opinion is still far from unanimous on

[1] *Mem. G.S.I.*, **11**, **14**, **17**.
[2] *Mem. G.S.I.*, **40**, Pt. 3.
[3] *J. Proc. Asiatic Soc. Bengal*, **17**, **18**.
[4] *Quart. J. Geol. Soc.*, **9**, 189.

the question of the age or ages of the Red Marls, Purple Sandstones and Salt. One school of thought assigns an Eocene age to these,[5] while others agree with Wynne placing them in the pre-Cambrian group.[6] Dr. Pascoe's sequence is also given for comparison and reference.

COMPARATIVE TABLE OF FORMATIONS (*after Wynne*)[7].

		East Salt Range.	*West Salt Range.*	*Trans-Indus Ranges.*
Alluvian and sub-recent		Superficial deposits	The same	The same
Post-Tertiary ..		Pebble beds, conglomerates and clays in all.		
Pliocene - Upper Siwalik		Conglomerates and clays	The same	The same to the north
Miocene	Lr. Siwalik	Sandstones and red clays	The same	The same
	Murree	Greenish sandstones	The same with red clays slightly present	The same with red clays slightly present
Eocene		"Upper Limestone"	U. Nummulitic olive clays, limestone, &c.	The same traces only
			L. Nummulitic limestones	The same
Cretaceous ..		Olive Series, red and white sandstones, &c.	White sandstones	Absent
Jurassic		Light coloured limestones and red and white sandstones	Absent	Upper limestone Lr. variegated sandstones
Trias		Salt pseudo-morph zone, sandstone clays	Absent	Absent
		Ceratite Beds, grey limestones	The same	The same
Carboniferous ..		"Lower Limestone"	The same	The same
Infra-Carboniferous		Speckled Sandstone	The same	Absent
		Boulder Beds	The same or similar	The same with some gypsum
		Magnesian Sandstone	Absent	Gypsum and Dolomite
Silurian (?)		Obolus Beds—shales	Absent	Absent
		Purple Sandstone	The same	The same
		Saline Series	The same	The same

(*After Pascoe*[8].)

Age.	*North.*	*South.*
Recent ..	Gravel and Alluvium	The same
Pleistocene ..	Conglomerate	—
Uppermost Pliocene to Tortonian	Siwalik	Siwalik

[5] *Proc. Geol. Soc. London*, 7, 39. *Mem. G.S.I.*, 40, Pt. 3, 356-370.
[6] *Mem. G.S.I.*, 10, 14, 17. *Rec. G.S.I.*, 50, 260, *et seq.*
[7] *Mem. G.S.I.*, 10, 14, 17.
[8] *Mem G.S.I.*, 40, Pt. 3, 337.

COMPARATIVE TABLE OF FORMATIONS (*After Pascoe.*)—*Continued.*

Tortonian to Helvetian	Kasauli	Murree		Absent
Helvetian to Burdigalian	Dagshai			Absent
Eocene ..	Nummulitic	U.	U. Chharat L. Chharat	Traces only
		Lr.	Hill Limestone	Hill Limestone (thin)
			Pisolitic and Ferruginous beds and sandstones	"Cardita beaumonti"
Eocene or Cretaceous	Grey Limestone			—
Cretaceous ..	Orange Limestone Giumal sandstone			Cretacious (thin)
Jurassic ..	Jurassic (including Spiti Shales)			Jurassic (middle or upper)
Trias	(?) Trias			(?) Ceratite Beds (lower)
Infra-Trias ..	Permo-Carb.	Infra-Trias		Productus Limestone
				Olive Series-Speckled S.s.
	U. Carb. ..			Conularia Beds
	U. Cambrian			Salt Pseudo-morph Series
	L. Cambrian			Magnesian S.s. series Neobolus Beds
Pre-Cambrian	Attock Slates			—

On comparing the above tables, it will be noticed there are several points of difference. No salt marls or Purple sandstones are mentioned in the latter, though it is clear from the text that Pascoe assigns these beds to the Lower Chharat Group.[9] Since Wynne's time the Neobolus Beds have yielded trilobites and Hyolithes, indicating a Cambrian age for these beds.[10] Wynne remarks as follows :—

"The whole of this great series from the red marls up to the post-Tertiary group presents a general and regularly successive parallelism of stratification, each group succeeding the one it rests upon without the intervention of any marked erosive action."[11]

Middlemiss reviewing this series says :—

"Where else can be seen a body of horizontal strata comprising members of the Palæozoic, Mesozoic and Cainozoic groups lying one above the other *in a single cliff section*[12] and apparently as unbroken by great uncomformabilities or by volcanic intrusions, as if they had just been formed? Where else does the geological

[9] *Mem. G.S.I.*, **40**, Pt. 3, 363.
[10] *Rec. G.S.I.*, **22**, Pt. 3.
[11] *Mem. G.S.I.*, **14**, 70
[12] Italics by writer.

record from Cambrian times upwards, present us with a set of rocks unaltered by metamorphism, undisfigured by chemical or dynamical changes, as free in fact from the dust of time as an uncut volume fresh from the binder's hands ? "[13]

Again Pascoe says :—

"There is something breathless about most of the geological indications in this corner."[14]

In this paper, the writer hopes to show that far from there being "a general and regularly successive parallelism of stratification," the very reverse is found, and it is hoped that this work will remove many of the difficulties that have hitherto presented themselves in the attempts to elucidate and explain the stratigraphy and structure of these hills.

Description of the Tertiary Strata.

As the principal groups of rocks met with in the areas mapped on the large scale belong to the Tertiary period, these beds will now be described in some detail. The lowest Tertiary rock in Dr. Pascoe's list is the Grey Limestone, which he assigns to either the Cretaceous or Eocene. This rock is absent in the regions under consideration.

Basal Beds of the Nummulitic Series.

Wynne describes the base of the Nummulitic group as follows :—

"The lowest part of the group is generally formed of rudely concretionary pale yellowish marly beds of great thickness with some beds of light coloured friable sandstones, grey shales and hematitic layers. Immediately below the marly limestones there is a dark band of gypseous shales, very commonly, but not constantly developed ; in these occur the Salt Range coals in strings and beds of very variable thickness and inconstant character. Just beneath the coally shales are sometimes a few beds of friable white or red or olive sandstones with grey shales interstratified. . . . Frequently the base of the whole formation is marked by a variegated white and red clayey hematitic band, which oft assumes the character of pisolitic hematite or the brownish look and polished surface of earthy laterite.[15]

Pascoe describes these beds as follows :—

"The grey limestone is succeeded by a thin band 2–20 ft. thick of variegated sandstones containing locally a bed of carbonaceous clay in which coal occurs to a limited extent. A pisolitic ferruginous band at its base resembles one at the base of the Subathus,

[13] *Rec. G.S.I.*, 24, 19.
[14] *Mem. G.S.I.*, 40, Pt. 3, 361.
[15] *Mem. G.S.I.*, 14, 105.

but it is probably older. The coal in one place reaches 17 ft. in thickness, but it and the carbonaceous band *usually show much crushing and shearing* and appear absent over wide areas. A corresponding zone is commonly found in the Salt Range, and comprises a basal hematitic band often pisolitic or lateritic and sometimes absent, followed in places by variegated sandstones or a dark foraminiferal limestone, above which come more constant gypseous shales containing strings of coal. 'Cardita beaumonti' characterises the shales, and plant fragments are common. The thickness varies from 50–150 ft."[16]

Both the above writers refer to hematitic layers in this basal group. None were found in the areas mapped in detail by the writer, but, during the examination for correlation purposes of other localities, such beds were seen. In the Bakh Ravine between Nammal and Musa Khel in the western Salt Range a lateritic rock was found in this position. The following description of the basal Nummulitic beds here is given from my report on the Kundal oil shows:—

"In this locality the rocks are more disturbed than at Mulla Khel (in the Maidan Range), but less so than at Kundal. The over-thrusting here was from the East. The Nummulitic limestones are similar to those of Mulla Khel, but between the basal nodular beds and the upper cherty bands, a shaly horizon is developed. In this latter is evidence of the over-thrusting of the upper beds. The junction of the basal nodular beds with the coal-bearing series appears to be normal. This latter series is more shaly than at Mulla Khel or Kundal, and there are numerous sandstone bands with fossil wood interbedded with the shales and coally shales. The whole has a thickness of about 200 ft. They in turn rest upon a lateritic bed, which upon close examination is seen to be a weathered lava similar to that found at Mulla Khel. Hence in this locality also there was a break between Mesozoic and the coal-bearing beds."

The section at Mulla Khel is interesting in this connection, and the following description is taken from the same source as the above:

"The rocks are much less disturbed than at Kundal. The Baroch River flows from the Maidan on the plain in Kohat beyond the range, and cuts through the hills giving wonderful sections of the strata. The sequence is as follows:—

Recent	Conglomerates
U. Siwalik	Grey sandstones
L. ditto	Red and purple sandstones with shales
Eocene	Nummulitic Limestone
ditto (Lakki ?) ..	Sandstones and shales with coal.
Jurassic or Triassic	Mesozoic Limestones.

[16] *Mem. G.S.I.*, **40**, Pt. 3, 343.

"The Nummulitic limestones form a large waterfall in the Baroch valley and are about 200–300 ft. thick. The upper portion consists of cherty limestones similar to those of Kundal. Below these are about 100 ft. of bluish grey nodular argillaceous limestones, which are absent at Kundal. These appear to pass gradually downwards into a calcareous sandstone with coal seams. This sandstone is identical with the oil sandstone at Kundal, except that it here contains fossil wood and some sulphur, the latter being due to the breaking down of iron pyrites. There are two massive beds of sandstone with interbedded seams of coal and shales. There are six seams of coal in all, the thickest being about eight feet. The whole group has an aggregate thickness of about 250 ft. Below these beds is a well marked horizon of green lavas,[17] of which two or three distinct flows can be detected by the presence of thin bands of sandstone crowded with the remains of belemnites and ammonites, evidently killed by the igneous outpouring. That there is a break here in the continuity of deposition is indicated by the absence of the brown oolitic rock met in the Kundal area."

This basal series has been described at length as they prove that:—

(*a*) An unconformity occurs at the base of the series.

(*b*) Igneous intrusions and extrusions occurred shortly before their deposition.[18]

(*c*) Conditions during their deposition were favourable for the accumulation of vegetable matter; and later it will be shown that there are excellent reasons for believing that this is the true oil horizon.[19]

It is interesting in connection with (*a*) to note that Mr. Nuttall has proved a similar unconformity at this horizon in Sind.[20] It will be noted that a Lakki age has been suggested for these basal beds, although they also bear some resemblance to the Ranikot Beds.[21] In the three areas mapped these beds are little exposed, and when they are present, are so fractured and disturbed that no generalisations may be drawn concerning their normal relations.

Hill Limestone.—Above the basal beds is a well-bedded massive more or less magnesian limestone. It is frequently unfossiliferous, but in a few localities has yielded nummulites. It is usually grey

[17] *Note.*—Similar Igneous rocks occur at Kundal, but as intrusives in the Trias.
[18] *Man. of Geol. (Oldham)*, 2nd ed., pp. 353-4.
[19] See pp. 494-496.
[20] *Quart. J. Geol. Soc.*, 81, Pt. 3, 426-8.
[21] *Geol. of India (Wadia)*, p. 216.

or drab in colour and often cherty. It weathers with a peculiar castellated appearance forming bold hill features, hence the name. I have mapped it as the Lower Nummulitic limestone. It varies greatly in thickness, being at least six hundred feet in Kohat, and only one to two hundred feet thick in the Khasor Range. The upper portion of the Hill limestone in many localities becomes intercalated with Carbonaceous shales, and passes gradually into a shale series with thin limestone bands. The limestones of this group are fossiliferous yielding nummulites.

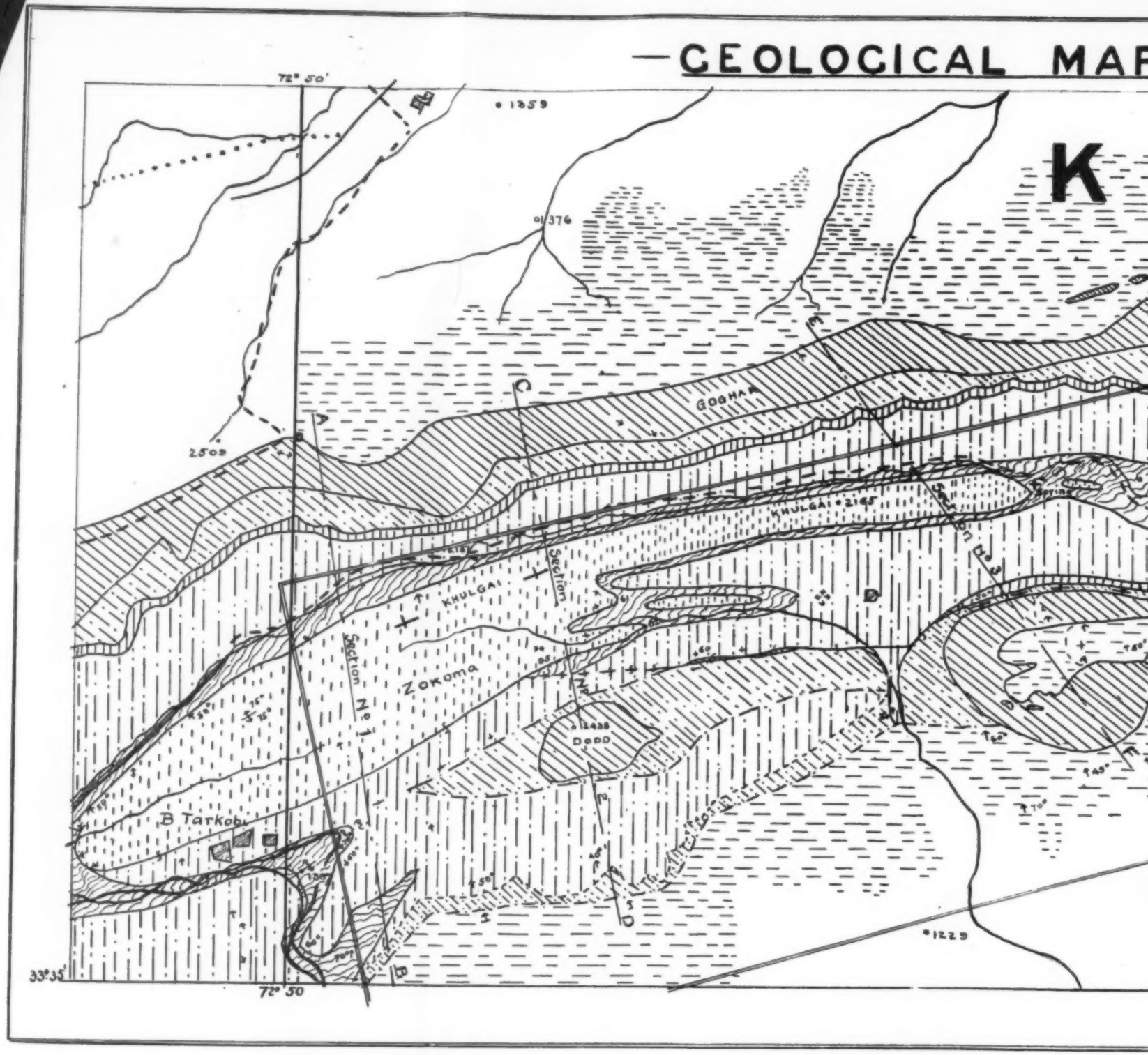
Green Shales.—The above beds pass gradually into pale olive sandy shales with thin limestone bands very like those below. The shales attain a considerable thickness especially in the Kohat Hills where they are about four hundred feet thick. They usually have the structure known as "Paper Shales," and are exceedingly friable. In the Salt Range this and the group below are very much more calcareous, the shales appearing as thin parting planes between the limestones.

Nodular Limestones.—Above the shales are about two hundred and fifty to four hundred feet of light grey massive Nummulitic limestones, which are often nodular in character. Associated with these beds are numerous layers composed entirely of oyster shells.

Gypsiferous Beds.—The Nodular limestones are succeeded by dark grey shales very rich in gypsum and containing considerable quantities of sulphur. As traced upwards they pass into red marls with a little gypsum. The marls are peculiar in that, except where they are associated with gypsum, they do not show any stratification. Griesbach reports in the Narai Sar hill of the Safed Koh Range some purple sandstones above these red marls, but none were found by the writer in any of the localities he mapped.[22] The thickness of this group varies enormously, in some places only forty feet of these beds being present, whereas in others as much as five hundred feet are noted. If these be the equivalent of the Salt Marls of the eastern Salt Range, they there attain a thickness of fifteen hundred feet.[23]

Upper Nummulitic Limestones.—This group overlies the gypsum beds; and three subdivisions are recognisable. The lowest consists of massive Nummulitic limestones with large nummulites and a few oyster beds. These beds are light to medium grey in colour, and can only be distinguished from the lower limestones by the large size of the nummulites they contain. Above these are green calcareous shales very like the lower group, but differing in that they are made up entirely of fragments of nummulites. The shales are

[22] *Rec. G.S.I.*, **25**, 102.
[23] *Mem. G.S.I.*, **14**, 71.


—GEOLOGICAL MAP
K
72° 50'
1359
1376
2503
GOGHAR
KHULGAI 2145
KHULGAI
Section
Section No 1
Zokoma
2428
DOPO
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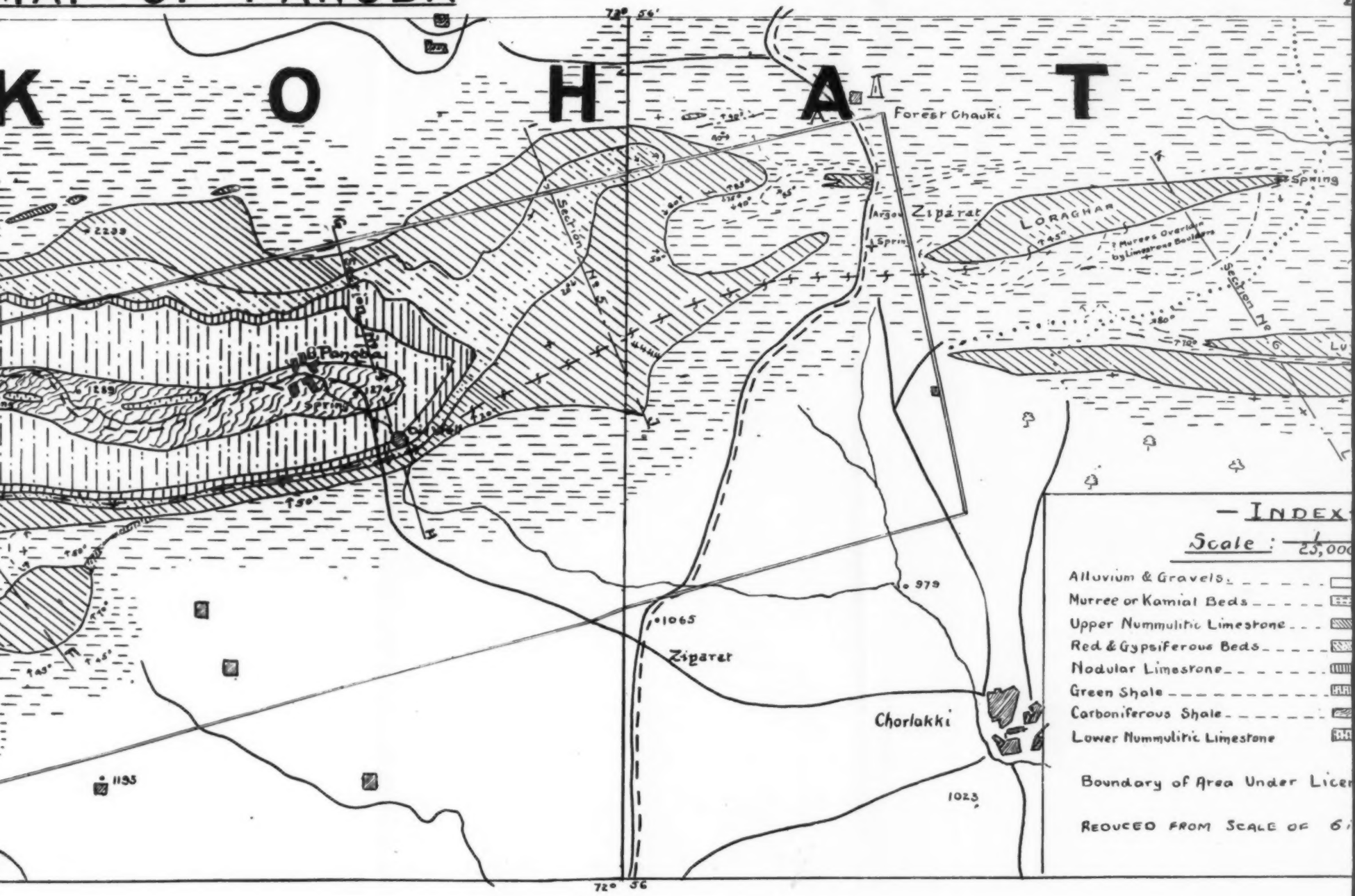
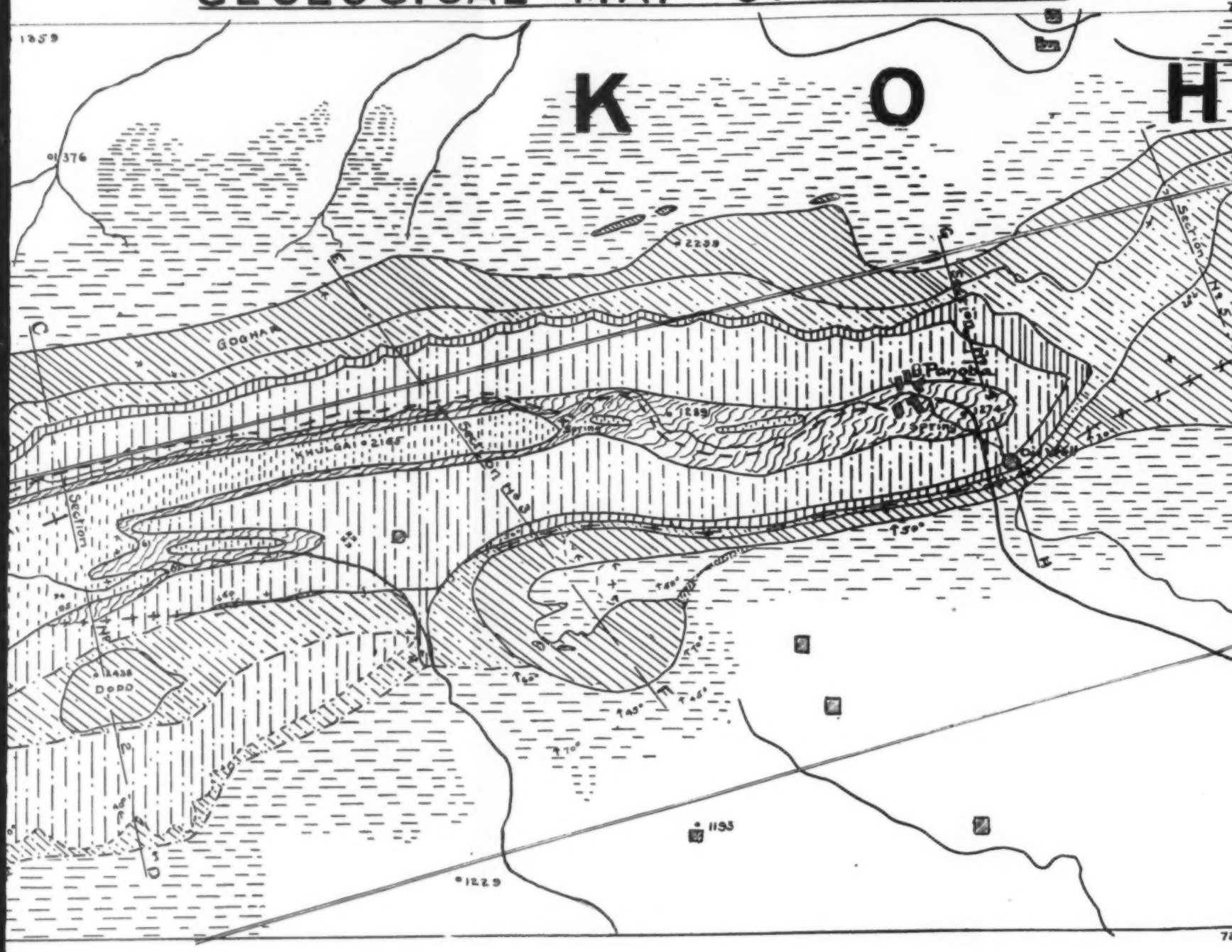
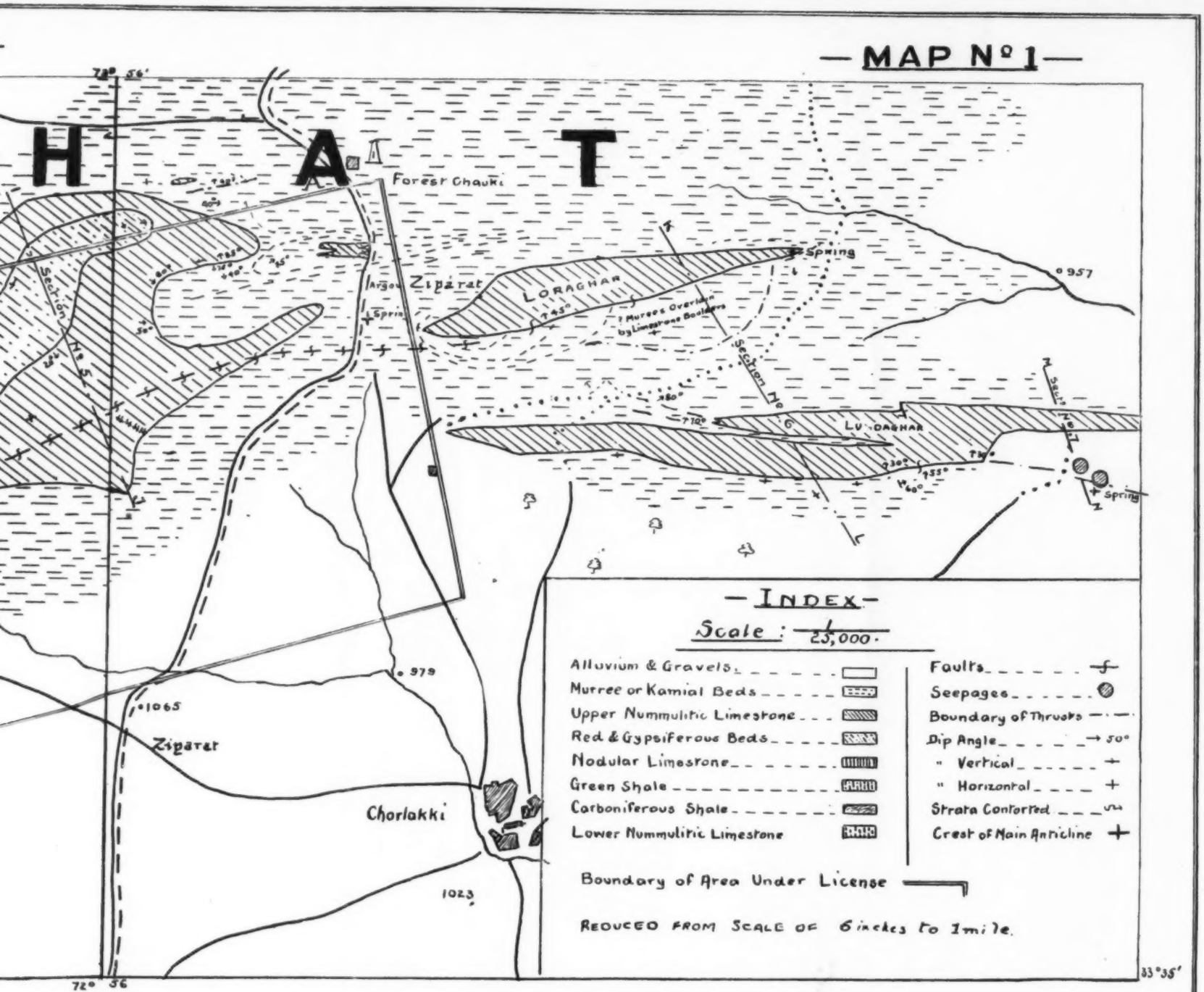
1229
33°35'
72° 50
A
B
C
D

MAP OF PANOBA — — KOHAT



—GEOLOGICAL MAP OF PANOBA—




— MAP Nº 1 —
H A T
72° 56'
Forest Chauki
Ziparat
Spring
LORAGHAR
957
? Murees Overlain by Limestone Boulders
Section No 5
Section No 6
LUNDAGHAR
979
1065
Ziparat
Chorlakki
1023
72° 56
33° 35'
— INDEX —
Scale : 1/25,000.
Alluvium & Gravels
Murree or Kamial Beds
Upper Nummulitic Limestone
Red & Gypsiferous Beds
Nodular Limestone
Green Shale
Carboniferous Shale
Lower Nummulitic Limestone
Faults
Seepages
Boundary of Thrusts
Dip Angle → 50°
" Vertical
" Horizontal
Strata Contorted
Crest of Main Anticline
Boundary of Area Under License
REDUCED FROM SCALE OF 6 inches to 1 mile.

succeeded by less massive Nummulitic limestones often with an oolitic structure, and characterised by exceedingly large nummulites. Some of the oolitic beds are yellow to golden in colour. Mr. Pinfold who has examined the above groups in great detail at Fatehjang, has suggested the following classification of this Upper Nummulitic Series.[24]

Upper Nummulitic Series	Upper Chharat Stage	Upper Limestones including the Nummulite Shales
	Lower Chharat Stage	Red and Grey Gypsum Beds
		Limestone with Planorbis
		Green shales[25]

In that area the Lower Chharat stage is a fresh water deposit, while the Upper Chharat is of marine origin. In the portion of the Trans-Indus Range examined by the writer the full sequence is not found, only the Lower limestones being represented. The sequence is well developed in the Kohat Hills, and although much more calcareous is also recognisable in the west Salt Range.

Murree Beds.—Above the Nummulitic group in Kohat are an extensive series of grey to green sandstones with intercalated red and purple shales and some dark brown conglomeratic beds, which Wynne describes as "pseudo-conglomerates."[26] These are mapped by both Wynne and Pascoe as Murree beds.[27] In the western Salt Range a similar group of rocks indistinguishable by the writer from the Kohat series is mapped as Kamlial (Lower Siwalik).[28] The writer has shown these beds in both areas as Murrees, but as there is no fossil evidence, the arrangement is open to doubt. Similar beds in the Fatehjang district have yielded a considerable vertebrate fauna which has led Dr. Pilgrim to classify the beds as Murree.[29] In the eastern Salt Range, however, similar beds have yielded a vertebrate fauna, which characterises them as of Siwalik age.[30]

Siwalik Group.—In every case where the writer has seen the Siwalik beds, their junction with the underlying rocks was a disturbed one. In other areas it has been established however that there is a perfectly conformable sequence. This group is extensively developed in these hills, where it consists of "a great thickness of fine-grained grey micaceous pepper and salt sandstones interbedded with clays near its lower portions, while the upper part of the system

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[24] *Rec. G.S.I.*, **49**, Pt. 3. *J. Proc. Asiatic Soc. Bengal (N.S.)*, **14**, 1918.

[25] Since the above was written, a paper by Major Davies suggesting a Lakki Age for the major portion of the Chharat Series, has come to hand. (See bibliography.) E.P.

[26] *Mem. G.S.I.*, **14**, 110.

[27] *Mem. G.S.I.*, **10**; **40**, Pt. 3, plates 70-80.

[28] *Mem. G.S.I.*, **40**, Pt. 3, plates 70, 80, 87.

[29] *Mem. G.S.I.*, **40**, Pt. 3, 375-6. *Rec. G.S.I.*, **43**, plate 26.

[30] *Mem. G.S.I.*, **40**, Pt. 3, 432.

is composed of soft sandy clays indistinguishable from the alluvium of the plain except by the disturbance they have undergone."[31]

Pleistocene or recent.—In addition to the dark-brown conglomerates of the Murree (or Kamlial) age, there are others identical with them, which must be of considerably later age, probably post-Tertiary. Some rest in a disturbed condition on Siwalik beds, and others on rocks of varying ages with little or no disturbance. Lithological characters of themselves are of no avail in the determination of the age of these, and unless they occur in close proximity to Siwalik beds it is impossible to determine their age.

Probable unconformity between Nummulitics and Murrees.—Wynne declared that everywhere in this region there was a conformable passage from the Nummulitic to the Murree group.[32] Medlicott, however, working in other areas had found a persistent unconformity at this horizon.[33] According to paleontological evidence to hand since Wynne's time, in many localities where that worker imagined a conformable sequence, it is proved there is an extensive time gap; equivalent to that of the whole Nari stage.[34] No definite discordance of dip or other stratigraphical evidence of such unconformity can be found in the localities examined. In a number of places, however, the basal bed of the Murree (Kamlial) group is a conglomerate containing limestone pebbles with large nummulites. This would indicate that at the time of their deposition the Upper Nummulitic limestones were undergoing erosion, so that an unconformity must be here present also. In the synclinal areas north of Sokan near Jaba the sequence appears to be a perfectly conformable one, but the writer had not the opportunity of following up this question. This is an ideal locality in which to prosecute this study.

Detailed Geological Mapping.

We are now in a position to study the three geological maps on the scale of six inches equals one mile, which have been prepared by the writer.

Maps.—The whole of this oilfield was remapped topographically between 1910 and 1913 by the Topographical Survey of India. Through the courtesy of the Officer-in-Charge, the data secured during these later surveys were used in the preparation of the special six-inch maps printed for the writer. The use of these maps enabled one to elucidate structural features, the solution of which

[31] *Man. of Geol. (Oldham)*, p. 356.
[32] *Mem. G.S.I.*, **14**, 108-9. *Man. of Geol. (Oldham)*, p. 355.
[33] *Rec. G.S.I.*, **9**, 49.
[34] *Mem. G.S.I.*, **40**, Pt. 3, 349-50.

would have been difficult, if not impossible, on the one-inch scale. The maps were printed in two colours only, for economy; the roads, rivers, villages, etc., being shown in black and the contours in brown (see Maps 1-3.)

The following localities were geologically mapped :—

1. *Panoba area* covering about 16 sq. m. in the Safed Koh Range of the Kohat Hills.

2. *Jaba area* comprising about 12 sq. m. of the Tredian Hills in the western Salt Range.

3. *Kundal area* being about 12 sq. m. of the northern end of the Khasor Range in the trans-Indus Salt Range.

The Panoba Area.

The area, so called from the hamlet of that name, lies on the right bank of the River Indus in the Kohat District, and extends westwards to the boundary of the Independent Territory of the Afridis near Narai Sar. It comprises a number of small parallel ranges of hills running in an East and West direction and forming the eastern end of the Safed Koh Range. The hills consist mainly of nummulitic limestone, rising from 1,000 to 1,500 feet above the plains to the north and south. The latter consist of Murree sandstones and interbedded clays, with a little recent gravel and alluvium.

Early Work Done.—The locality was first examined by Mr. Lyman, who reported to the Punjab Government on the occurrence of petroleum near Panoba village.[35] Mr. Griesbach, of the Indian Geological Survey, examined this range about 1890, and described the lie of the rocks and the structures developed.[36] In 1913 Dr. E. H. Pascoe, also of the Indian Geological Survey, remapped this region, having now the advantage of the new topographical survey maps on the inch scale.[37] The latter worker disagreed with the findings of Mr. Griesbach.[38] The former does not recognise any faulting of the beds, but explained the structure as "a steeply compressed sigmoidal anticline,"[39] which he regards as almost isoclinal. The latter recognised two very extensive lines of fracture, which, judged by his sections, he regarded as normal faults.[40]

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[35] *Rept. on Govt. Oil Lands (Lahore)*, 1870.
[36] *Rec. G.S.I.*, **25**, Pt. 2, 101, *et seq.*
[37] *Mem. G.S.I.*, **40**, Pt. 3, 410-2, plate 80.
[38] *Mem. G.S.I.*, **40**, Pt. 3, 410.
[39] *Mem. G.S.I.*, **40**, Pt. 3, 411-12.
[40] *Rec. G.S.I.*, **25**, Pt. 2, 101-5; Pt. 2, Figs 6-7.

Griesbach's sequence and description, with which my observations are in close accord, are given below[41] :—

Eocene	Upper	g. Sandstones and grits with subordinate limestone beds, prevailing colour of sandstones red		Murree Group of Wynne
	Middle	f_4. Limestone beds of Narai Sar ranges containing nummulites	Subathu (?)	
		f_3. Purple red sandstones and shales of Narai Sar. 600-700 ft. thick		
		f_2. Limestone with reddish patches containing nummulites. 500 ft. thick		
	Lower	f_1. Dark crumbling shales with limestone partings. 400 ft. thick		
		f. Hard dark limestone with nummulites. 1200 ft. thick		

" Both in the Panoba and Tarkhobi valleys the sequence may be observed. The nucleus, as it were, of the section is formed by hard grey limestone (f), which is greatly disturbed—dipping from 60°–80° to the north below the shales. (f_1) A double ridge of this limestone runs between Tarkhobi and Panoba, showing a steep dip slope along its whole northern side. This limestone ridge is greatly jointed and *shows at least two long lines of fault.*[42] The northern one is much crushed producing no great throw either side, whereas the southern one forms the boundary between the nummulitic limestone and the red (Murree) sandstone beds (g). The rest of the section is simple. About a quarter of a mile west of Panoba village some lenticular deposits of the shales (f_1) are interstratified between massive beds of the nummulitic limestone. (f) The latter is raised vertical, but the dip gradually lessens westwards to 65°, varying considerably at short distances. The shales being easily disintegrated have been denuded away along the strike of the beds ; hence the longitudinal valleys of Panoba and Tarkhobi, which are separated by a low saddle about half-way between the villages. The shales rest conformably on the limestone (f) ; they vary considerably in lithological character from greenish clay shales, in which indistinct fucoid markings are discernible to very dark alum shales. . . . The limestone forms a crushed fold in the Tarkhobi valley, the dip turning round from N.W. to S.W. Round this termination of the crush fold, the shales (f_1) are placed conformably to the former ; and in a loop of the ridge of the Narai Sar, which corresponds to the fold of the limestone, the ascending section from the shales to the Murree Series is very plainly seen. The top of the Narai Sar Ridge is formed of the Upper Eocene limestone (f_4), which also contains

[41] *Rec. G.S.I.*, **25**, Pt. 2, 102-3.
[42] Italics by writer

nummulites in every bed, and this division is conformably overlain by the Murree Series (*g*). Panoba village, itself, stands on the shales (f_1), which contain a good deal of gypsum in leaflets. The shales have some partings of flaggy limestone, breaking with a conchoidal fracture; they are overlaid by hard grey limestone (f_1), which contains many minute remains, mostly foraminifera and distinct nummulities. North of Panoba the sandstone beds, which are best seen in the Narai Sar Section, are replaced by brown and olive shales with thin bedded marls and a few sandstone beds, which are best seen in the Narai Section. With these are thin bedded marls and a few sandstone bands. This division is followed by the Upper Nummulitic limestone (f_4) of the Narai Sar Range. The dip is very rolling. The beds which form the Narai Sar Range dip pretty steadily 40–45° N.W. and N. On the other hand, the shales (f_1) are greatly crushed, and the limestone ridge between Tarkhobi and Panoba is formed by crushed limestone beds. Near the south-western portion (Fig. 7) the limestone (*f*) dips below the shales under an angle varying from 60–80°, whilst at Panoba this bed is nearly vertical; and about 200 yards below the village has turned to the south-east about 74°, but this varies a great deal more nearer the fault, which may be traced along the entire southern slope of the well-marked double ridge between Panoba and Tarkhobi. . . . About half-a-mile below the village of Panoba the limestone shows evidence of great crushing, and at least two clear faults may be seen, no doubt the continuations of the Tarkhobi dislocations. There in the joints close to the northern line of fault some oil oozes out in thick drops, which collect on the surface of three pools. With it issue very small springs charged with sulphuretted hydrogen gas. . . . Some 150–200 yards further south-east, the great fault shown in both sections (Figs. 6 and 7) has cut off the limestone and brought it in direct contact with the Murree beds (*g*). The fault is best and clearest seen on the right side of the valley, immediately below the oil springs; it is accompanied by a great deal of minor disturbance and crushing of strata. Some 70–90 ft. of the section is entirely formed of slipped crushed masses, whilst the dislocation is partly filled by a very distinct faultrock—a breccia of limestone and red sandstone blocks and debris cemented by a calcareous matrix. The same may be observed near Tarkhobi W.S.W. of the oil springs."

Stratigraphy.—Narai Sar was not within the area mapped on the six-inch scale. The purple and red sandstones and shales (f_3) of Griesbach are undoubtedly the red gypsiferous shales shown on map No. 1. The large scale work has proved that the dark alum shales (my carbonaceous shales) are not a lateral variation of the green shales as above stated, but are lower beds underlying the

latter. Owing to his not having realised this, Griesbach did not recognise the amount of the throw of the northern fault at Tarkhobi, though he was aware that there is a dislocation of the strata here. It is remarkable that Griesbach did not describe these faults as over-thrusts, as he states in the same work that the geological structure of the Safed Koh Range is "that of a succession of reversed flexures, their long shoulder dipping northwards and divided by at least two great systems of dislocation."[43]

The above description of the succession here was not seen by the writer until long after his mapping work was done, and is the more interesting because it is in so close accord with the present results.

In the mapping of the area on the six-inch scale the following succession was recognised :—

7. Murree or (Kamlial beds).
6. Upper Nummulitic limestone.
5. Red and gypsiferous clays.
4. Nodular Nummulitic limestones.
3. Green shales.
2. Carbonaceous shales.
1. Lower Nummulitic limestones.

The above sub-divisions agree with those mapped by Pascoe except that his group 4 is "a thin clay band on an ochreous sandstone." Such a band was not found by the writer, but from Pascoe's text it is clear that his group 4 lies in or near the nodular limestones.[44]

Distribution of the Groups.

Lower Nummulitic Limestone.—The Lower Nummulitic limestone is the lowest strata, exposed, and nowhere is the base of the division seen; hence it is impossible to arrive at the thickness of this formation in this locality. The Geological Survey report a maximum development in any area at 1650 ft.;[45] but not more than 500–600 ft. are here exposed. It will be noted that both Pascoe and Griesbach give a greater thickness than the above (1200 and 1300 ft. respectively).[46] This is because they regarded the anticlinal fold north of Tarkhobi as a simple one, whereas this work has proved it to be a complex one of three anticlinal folds. They are practically vertical or overturned to the south and dipping very steeply to the north. The beds appear to be

[43] *Rec. G.S.I.*, **25**, Pt. 2, 105.
[44] *Mem. G.S.I.*, **40**, Pt. 3, 410-1; plate 80.
[45] *Mem. G.S.I.*, **40**, Pt. 3, 344.
[46] *Mem. G.S.I.*, **40**, Pt. 3, 41. *Rec. G.S.I.*, **25**, Pt. 2, 102.

unfossiliferous, though both Pascoe and Griesbach reported nummulites from this group. They are only found outcropping in the Main Dome (Khulgai) north of Tarkhobi village, in the main hill, and in two small outliers to the east between that village and Panoba. They have suffered considerable earth-movement.

Carbonaceous.—The uppermost portions of the above-subdivision show interstratifications of black shales, and the limestones become less massive and contain numerous nummulites. The shales with the thin limestone bands attain at least 250 ft. vertical thickness near Panoba village, where is found their greatest development. They occur along the entire northern face of the Khulgai ridge and are extensively developed at the eastern end between Panoba and Tarkhobi. They are cut out by the northern fault north of Tarkhobi village, but reappear on the south side of this fault in the nulla bed below Tarkhobi village (see Fig. I). Their crumpled and fractured state at the eastern end of the outcrop near Panoba village is well shown on Fig. 2. They pass gradually into the overlying group.

Green Shales.—The Green shales outcrop very extensively within the main dome, and are also present between the two thrusts, from the Tarkhobi Nulla in the West to the Khulgai Nulla. They attain a thickness of about 400 ft., the lower 250 ft. consisting of soft olive green shales, characterised by the structure known as "Paper Shales." The upper portion contains intercalated with these shales thin flaggy limestone beds invariably crowded with nummulites and a few oyster beds. They have suffered considerable disturbance and especially at the eastern end of the limestone ridge between Tarkhobi and Panoba have a decided rolling structure. Fig. 3 shows an asymetrical anticline developed in these beds in the Khulgai Nulla in the outcrop between the two great thrusts.

Nodular Limestones.—The nodular limestones are light to dark grey massive limestones containing nummulites and some oyster beds. The nodular or concretionary character is probably due to earth-movements altering limestone beds with thin shaly partings. Such alteration is clearly visible in other areas, where the change has apparently not progressed so far as in this locality. Their position underlying a thick plastic clay group has resulted in their being considerably crumpled and contorted. They attain a thickness of about 150–200 ft. in the eastern portion of the Main dome, where alone they outcrop. They are absent along the south-eastern boundary of this dome, being cut out by the northern over-thrust. They come in along this thrust plane a little west of the Khulgai Nulla.

Red and Gypsiferous Beds.—Above the concretionary limestone are some dark grey clays very rich in gypsum and with patches

of sulphur crystals. They are succeeded by red clays with a little gypsum. The most remarkable feature of this division is their variable thickness, which could not be the result of varying deposition; but is undoubtedly due to their having been squeezed from places of high to those of low compression. The presence of such plastic clays with such a large gypsum content intercalated with massive limestones, has determined the complexity of the structures developed in these and the overlying series by the earth-movements. These red clays are characteristic of almost every thrust plane that has been mapped,[47] and they have doubtless been squeezed along such lines of fracture and facilitated the displacement of the strata. The springs below this sub-division are almost invariably sulphurous. The salt deposits of the Kohat Hills are found in association with these clays, but no salt occurs in this locality. Their maximum vertical thickness here is about 200–300 ft. Their greatest outcrop is in the eastern end of the Main dome, but they also occur extensively in the tract between the two great thrusts, and almost everywhere on the line of the southern one. Fig. 4 shows the gypsiferous variety acutely folded in the latter position.

Upper Nummulitic Limestones.—The uppermost division of the Eocene series is the Upper Nummulitic Limestone, which outcrops extensively forming every range except that between Tarkhobi and Panoba. Three sub-divisions were recognised; a lower group of massive grey limestones rich in nummulites, and capped by an oyster bed, and often nodular; a middle one of green shales very like the lower shales but consisting almost entirely of fragments of nummulites; and an upper group of fairly massive limestones some shaly and concretionary and all characterised by nummulites of large size. Frequently the latter sub-division is capped by an oolitic band, often yellow to golden in colour. The middle division is of variable thickness. The whole group attains a thickness of between 500–700 ft.

Murree (or Kamlial) Beds.—The plains both north and south of the ranges consist entirely of sandstones, usually greenish in colour, intercalated with red and purple clays and dark brown conglomerates. Their general strike is east and west, and they dip at high angles to the north. Near the village of Jabbar, however, the dip is more gentle (about 45°). Where these beds are apparently in normal contact with the Upper Nummulitic limestones, it was noticed that the basal beds were conglomeratic and contained pebbles of the above limestones with derived nummulites. It

[47] See Map. 1, particularly along Southern Thrust between Tarkhobi and Panoba Nulla.

FIG. 1.

BLACK SHALES S. OF NORTHERLY THRUST. LOWER LIMESTONE RIDGE BEHIND. IN TARKHOBI VALLEY.

FIG. 2.

BLACK SHALES SHOWING CRUMPLING AND FRACTURING OF THIN LIMESTONE BANDS. W. OF PANOBA VILLAGE.

FIG. 3.

ASYMETRIC ANTICLINE IN GREEN SHALES IN KHULGAI N.

FIG. 4.

CONTORTIONS IN GYPSUM BEDS ALONG SOUTHERN THRUST ON S. SLOPE OF HILL 2438.

FIG. 5.

SYNCLINE IN MURREE BEDS.

Note dip of axis to E. S. Slope of Kamtara Ridge West of Panoba Gorge (looking East).

FIG. 6.

FAULTED SYNCLINE IN MURREE BEDS IN PANOBA GORGE.

FIG. 7.

FIG. 8.

TWO VIEWS OF BRECCIATED ZONE IN NORTHERN THRUST IN PANOBA GORGE.

FIG. 8.
TWO VIEWS OF BRECCIATED ZONE IN NORTHERN THRUST IN PANOBA GORGE.

FIG. 9.

FIG. 7.

FIG. 10.

FIG. 11.

THREE VIEWS ALONG A N.–S. LINE ACROSS THRUST PLANE BETWEEN PANOBA GORGE AND ROAD.

A = Same tree in 9 and 10. B = Same outcrop of Murree Beds. C = Vertical Num. Limestone.
D = Murrees dipping 40° S.

FIG. 12.

JUNCTION (OVER-THRUST) NUM. LST. (A) ON MURREES (B) A LITTLE EAST OF PANOBA GORGE.

Note.—(A) does not outcrop in stream bed.

FIG. 13.

FIG. 14.

TWO VIEWS ON SOUTH FACE OF LIMESTONE OUTCROP NEAR FOREST CHAUKI, SHOWING "TEAR PLANE."

A = Limestone. B = Murree Beds. C = Camera case in same position while views were taken. (See also Map 1.)

FIG. 15.

KUNDAL—BASTI ALGAD—OVERTHRUST TRIAS ON CARBONIFEROUS.
D = Thrust Plane. A = Trias. B = Carboniferous. C = "Red and drab clays."

FIG. 16.

KUNDAL—BASTI ALGAD.
View showing Oil Sandstone wisp (A) caught up by overthrust "Red and Drab Clays" (B). (C) is Oil Seepage.

would seem, therefore, that here also in spite of the apparent conformity there was a break. Fig. No. 6 shows synclinal folding in these beds in the Panoba Nulla. They have been considerably disturbed. These rocks are identical with beds in the Jaba area[48], which Pascoe has mapped as "Kamlial" (*i.e.*, Lower Siwalik), Here he has mapped them as Murree.[49] As they are unfossiliferous this question of their true age could not be determined, hence the nomenclature in the margin.

Evidences of Faulting.

From the quotation given above,[50] it is evident that Griesbach recognised at least two very extensive lines of faulting. On the other hand Pascoe in his more recent work, definitely disagrees with the former, and does not recognise any fractures but explains the structure and distribution of the rocks by acute folding. The following list has therefore been drawn up showing the evidences that are available, that the folding has been so acute that it has resulted in fracture and displacement of the beds:—

(1) In many places the limestone beds are crushed, fractured and have a brecciated appearance (see Figs. Nos. 7-8).
(2) The presence of calcite stringers in the limestones near the thrust planes, especially at Panoba Gorge and at the south-east end of Hill 1475 is indicative of faulting.
(3) The limestone shows slickensiding at the above localities.
(4) The Murree Beds in the Panoba Gorge below the oil show are folded into synclines and anticles. These when traced northwards towards the limestone junction exhibit that there is not sufficient room for the whole suite of Murree beds, and that some must have been cut off by a fault (see Fig. No. 6).
(5) A massive limestone bed outcrops on the left bank of the valley but is not present in the bed of the stream in the Panoba Gorge (see Fig. No. 12). This is explained in Section No. 4.
(6) The Nummulitic (green) shales were found repeated in a north and south line across the range east of the oil seepage at Panoba (see Section No. 5).
(7) Murree beds south of Loraghar have a curved strike, when followed northwards along the strike, the Upper Nummulitic limestones cut across them almost at right angles (see Map 1).

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[48] *Mem. G.S.I.*, 40, Pt. 3, plate 87.
[49] *Mem. G.S.I.*, 40, Pt. 3, plate 80.
[50] See pp. 17-18.

(8) The absence of the Carbonaceous shales along the southern face of the Khulgai ridge behind Tarkhobi, and their presence in the Tarkhobi Nulla south of the village and almost to the Murree junction can only be the result of faulting (see Fig. No. 1).

(9) West of the Forest Chauki the Murree beds, which dip northwards about 40°, cut out some limestone beds on the same strike line. The limestones are almost vertical. This is clearly a "tear plane" (see Figs. Nos. 13–14).

(10) South of the Main Range a little west of the road evidence of faulting is clear in the three photos attached. (Figs. Nos. 9–11).

(11) The sections given by Dr. Pascoe do not and can not explain the non-continuance of his southernmost outcrop of limestone west of the Khulgai Nulla in an eastern direction. This cutting off of these beds can only be the result of faulting.[51]

It is clear from Griesbach's sections that he regarded the two fractures he traced as normal faults.[52] This is the more remarkable in that he recognised the structure of the range (*i.e.*, Safed Koh) was characterised by reversed flexures.[53] From the above data, photos, maps, and sections,[54] it is indisputable that fracturing has taken place here.

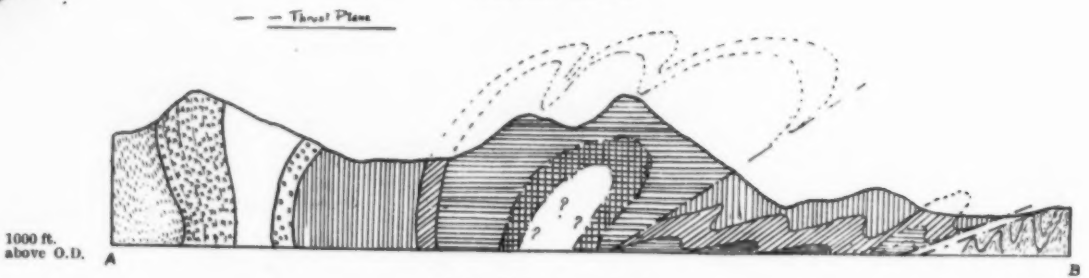
Structure.

From an examination of Map 1 and Sections 1–7 it will be seen that there is one large dome with two or three smaller ones to the east. The long axes of these structures have an east and west direction and are much longer than the north and south axes. The strata are very highly inclined having usually a steep dip towards the north. The structure is due to an intensive earth-movement, having a north and south trend and moving from the north. This tectonic force crumpled the beds into complex folds of the fan type and later squeezed these folds until the limbs became vertical or over-turned towards the north. This pressure was continued until the southern limbs of these folds fractured, and some of the northerly folds were over-thrust on to those to the south. Such folding and fracturing is represented diagrammatically in No. 8 sketch.[55] There is no doubt that the highly plastic gypsiferous clays have played an important part

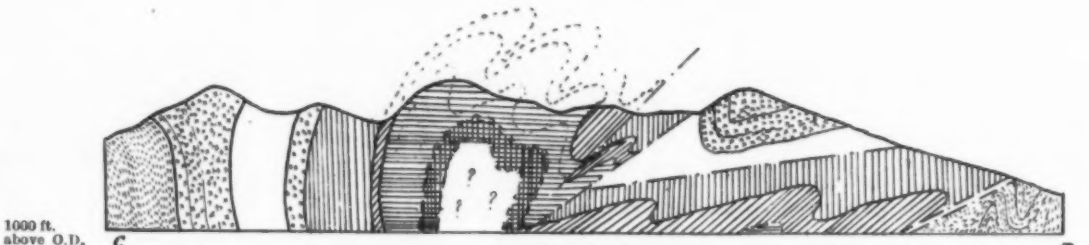
[51] *Mem. G.S.I.*, 40, Pt. 3, plate 81.
[52] *Rec. G.S.I.*, 25, Pt. 2, plate 2, Figs. 6-7.
[53] *Rec. G.S.I.*, 25, 105-7.
[54] See Map 1 sections).
[55] See Map 1 (sections).

MAP 1 (SECTIONS).

PANOBA AREA.

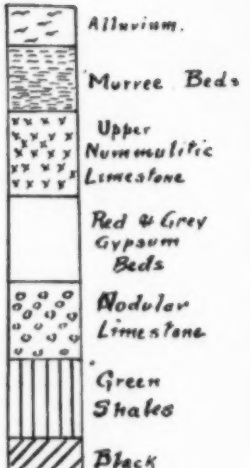


NO. 1 SECTION ALONG AB.

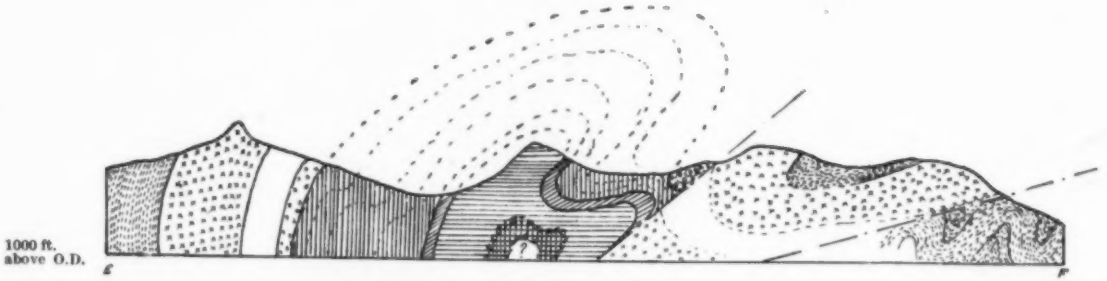


NO. 2 SECTION ALONG CD.

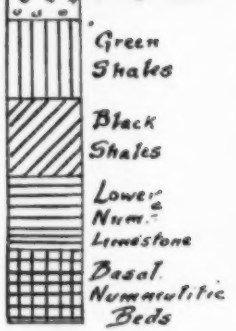
INDEX.

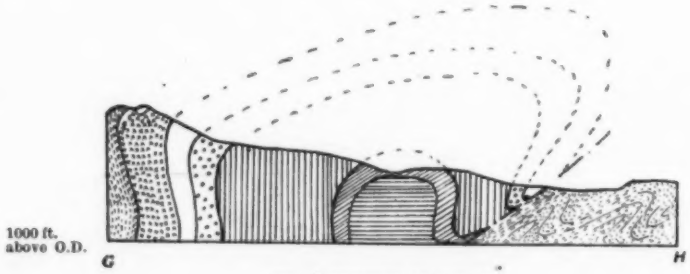


NO. 2 SECTION ALONG CD.

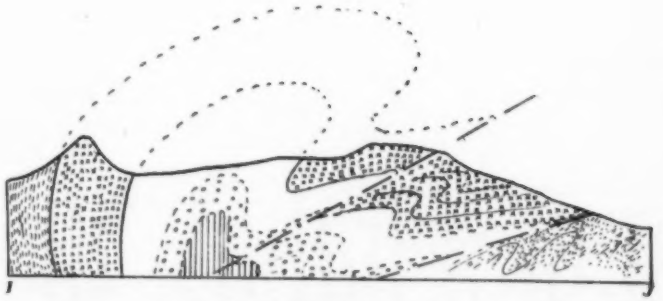


NO. 3 SECTION ALONG EF.

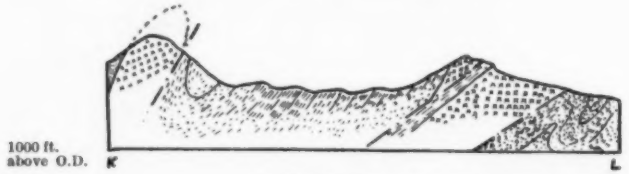




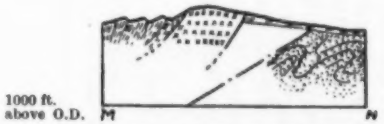
NO. 4 SECTION ALONG GH.



NO. 5 SECTION ALONG IJ.



NO. 6 SECTION ALONG KL.



NO. 7 SECTION ALONG MN.

NO. 8.—DIAGRAMS SHOWING DEVELOPMENT OF OVERFOLD INTO A THRUST.

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in determining the character of the folds and the over-thrusting of the beds. They have been squeezed into the crests of the anticlines (*e.g.*, the large extent of these beds east of Panoba village) and into the troughs of the synclines (*e.g.*, the wide exposure on Hill 1438) and have provided a suitable plane surface on which the over-thrust strata could glide.

The following domes and outcrops have been recognised and named from the local names of the hills or ranges to which they give rise :—

(1) Main or Khulgai Dome.
(2) Angou-Ziyarat Dome west of the ziyarat on the road across the eastern end of the area mapped.
(3) Loraghar Dome south-east of the above ziyarat.
(4) Lundaghar Outcrop in the extreme south-east of the area mapped.
(5) Small dome in the limestones cut off to the east by over-thrust Murrees, and situated west of the Forest Chauki. (See Figs. No. 13 and 14).

Khulgai or Main.—The Main Dome extends from the extreme south-west of the portion mapped near Tarkhobi village almost to the road above mentioned. In the extreme west the main axis has a direction from 240–260° E. of N. to 60-80° E. of N. As traced eastwards, it gradually swings southwards until at its eastern end it has a direction due east and west. The length of the dome is six and a half miles, while the shorter axes vary from three-quarters to one and a quarter miles. The main axis is not horizontal. Its highest point coincides with the peak a little N.W. of the village of Tarkhobi.[56] From this point it falls both east and west. To the east its fall for the first 8500 ft. is at an angle of about 8° to the horizontal. For the next 4500 ft. the fall is gradual with some oscillations, which account for the small domes of Lower Nummulitic limestone a little west of Panoba village. The axis then falls more acutely bringing in the whole of the Lower and Upper Chharat Beds in the next 9000 ft. This is equivalent to 1 in 7 or about 9°. Further east, the fall continues with some oscillations. To the west of the highest point of the axis the fall is about 9° to the horizontal and regular. Sections Nos. 1 to 5[57] are taken across this dome and show that it is by no means a simple structure. The main ridge a little north-east of Tarkhobi (Section 1) consists of a complex anticlinal fold, the southern limb of which was fractured and the fold thrust forward so that the Lower limestone rests on Green shales behind Tarkhobi. The country

[56] Between the two + on Map 1.
[57] See Map 1 (sections).

around Hill 2438 to the south of this thrust is a synclinal area in the Upper Nummulitic Series (Section 2). This has also been thrust on to an anticlinal in the Green shales, and this thrust must be of very low hade, as these beds (*i.e.*, the Upper Nummulitics) are not present in either the Khulgai or Tarkhobi Nullas, where the Green shales out-crop (see Fig. No. 3). The anticlinal is thrust forward on to the Murree beds and everywhere along this thrust plane more or less gypsiferous beds are found (see Photo No. 4). The Main dome is the only dome or outcrop in which beds below the gypsiferous beds are exposed. All the others consist entirely of the Upper limestones with a little of the gypsiferous strata and overlain by the Murrees.

Loraghar Dome.—In the Loraghar Dome the only beds exposed are the Murrees and the Upper limestones. The dome structure is normal and regular at the eastern and western ends and along the northern face, where the beds dip very steeply to the North. Along the southern face the limestone beds are cutting across the strike of the Murree beds as shown in Map 1. This is clearly an over-thrust but the amount of displacement is undoubtedly small. The structure of the Murrees between here and the main dome show that the whole series of limestones and Murrees were folded into domes and basins with steeply dipping sides, and that these were later fractured and over-thrust.

Lundaghar Outcrop.—The Lundaghar outcrop has not a dome structure. It is shown in Dr. Pascoe's map as such,[58] and the outcrop of the limestone is shown as terminating on the western bank of the Indus River. This is not so; the limestone outcrops in the river bed, and also on the left bank of the Indus in Punjab, where it gives rise to a small range of hills. An examination of the south-eastern corner of the outcrop shows that the gypsum beds occur in a thrust plane caused by the limestones being over-thrust on to the Murree beds. The limestones show great slicken-siding and the development of calcite. The western end of the outcrop is masked by alluvium, and on the northern face the Murrees dip steeply to the north. A thin outcrop of these beds also occur at the summit between two limestone bands; it could not be decided whether this was due to an isoclinal synclinal structure or to another over-thrust.

Angou-Ziyarat Dome.—The small dome structure near the Angou-Ziyarat is due to a roll in the axis of the main fold bringing up the limestones between the Main and the Loraghar domes. It has a length of about 1000 ft. and a width of 200 to 250 ft. It is terminated to the west by quaquaversal dips of the Murrees

[58] *Mem. G.S.I.*, 40, Pt. 3, plate 80.

which here have a marked basin structure with steeply dipping sides. The nulla section to the west shows that it is not a regular dome but there are three steep anticlinal folds. In the western end, however, only two such anticlinal folds can be traced. The southern face of this structure is not over-thrust, but the folds are over-turned to the south and the beds dip at high angles to the north; the limestones being overlain apparently conformably by the Murrees.

Outcrop west of Forest Chauki.—The outcrop west of the Forest Chauki is exceedingly interesting. In the westerly portion there is a very steeply dipping dome with a small limestone outcrop in the centre. To the east, however, the Murrees dip to the north at relatively low angles (45°). These Murrees cut off the limestone being clearly thrust southwards and the Murree-Limestone junction being a "Tear Plane." (see Figs. Nos. 13 and 14).

Thrust Planes.—The sections (Map 1 sections) attached show the complex anticlinal structures developed and the over-thrusting of these folds to the south. Three important thrusts were observed and mapped:—

(1) *The Northerly Thrust*, which brings the Lower Nummulitic limestone in contact with various higher members of the Nummulitic group.

(2) *The Southerly Thrust*, which brings various members of the Nummulitic group in contact with the Murree beds.

(3) *The Central Thrust*, which is responsible for the outcrop of the Upper Nummulitic limestones on Hill 2438, and of the same rock with Murrees on the Marachagnai Hill.

Northerly Thrust.—This fracture was noted by Griesbach,[59] though he failed to recognise any displacement here, as he regarded the Carbonaceous shales as lateral variations of the Green shales, whereas they underlie the latter. The thrust can be traced from a little west of Tarkhobi village eastwards between the Main or Khulgai ridge and the southern limestone range to the Panoba Gorge. Here it bifurcates and a small branch runs a little north of east in the Upper Nummulitic beds. The main one continues in a general easterly direction and forms the Nummulitic-Murree boundary almost as far as the road which crosses the area. Figs. Nos. 7 to 12 were taken along this junction. In the Chorlakki Nulla between the Main and the Loraghar Domes, it undoubtedly cuts the Murree beds, but as this group is a repetition of identical beds, the fracture is traced with difficulty. It is present south of the Loraghar Dome, where a roll of the anticlinal axis again brings up the Upper Nummulitics which are thrown against the

[59] *Rec. G.S.I.*, 25, Pt. 2, 102.

Murrees. East of Loraghar it cannot be traced in the Murree beds there outcropping.

Thrust not Parallel to Anticlinal Axis.—As will be seen from Sections Nos. 1 to 5 the line of the thrust is not parallel to the anticlinal axis, but has a general direction almost due east and west. Consequently the fracture cuts across higher members of the strata as traced from west to east; a fact also amplified by the easterly dip of the anticlinal, which was described on pp. 457–458. An examination of Map 1 shows the Lower limestone thrown in contact with the Green shales at Tarkhobi; further east the Black shales are in conjunction with the Green shales; while near the headwaters of the Khulgai Nulla the break occurs near the bottom of the Nodular limestone beds as shown by the small exposures of the latter along the thrust. In the Panoba Gorge the fracture occurs about the top of the Nodular group; and further east the Upper Nummulitics are brought in contact with the Murrees. The question arises, why is there such a small development of the gypsiferous clays along this Thrust? In order to understand this it is essential to realise another interesting feature of the fracture. In the west near Tarkhobi, the break is in the southern limb of an anticlinal fold in the Lower limestone (see section No. 1). As traced eastwards the line of thrust creeps down this limb until at Panoba it cuts across the trough of a syncline in the Nodular limestone and the gypsiferous beds (see section No. 4). Still further east it cuts across the southern limb of a syncline, as proved by the repetition of the Nummulite shales along a north and south line across the range about half a mile east of the gorge. This also accounts for the limestone band shown in Photo 12, not outcropping in the stream bed (see para. 5, p. 455). In the Panoba gorge section there is only about 100 ft. of the gypsiferous beds present. We have seen on p. 457 that these clays have been squeezed from the areas of relatively high to those of low compression; the acute syncline at Panoba gorge shown in the Section No. 4 is a region of relatively high compression. Consequently in the folding process before the fracturing occurred, the clays would be squeezed out of this portion of the fold; thus accounting for the limited occurrence of this group here, while only a quarter of a mile to the north-east, it is extensively developed.

The Southern Thrust.—This is the largest thrust developed in this area, and has given rise to the greatest displacement. We have no means of measuring the hade of the fracture. It is well exposed in the Tarkhobi Nulla and along the southern face of Hill 2438. At the former locality about one mile downstream from the village, it brings the Carbonaceous shales against the Murree Beds. The actual junction is marked by a massive lime-

stone bed, which Dr. Pascoe has mapped as the Upper Nummulitic limestone. It is undoubtedly one of the Nummulitic bands that occur commonly in the Carbonaceous shales. Dr. Pascoe has shown the Upper limestone along the entire southern junction of the Nummulitics and the Murree. No such limestone band is seen along the face of Hill 2438, where the Green shales with their intercalated limestone bands everywhere forms the junction. In this thrust plane there is a great development of the gypsiferous beds showing a highly folded and crumpled structure. Fig. No. 4 was taken along this contact. The fracture is not well seen in the Khulgai Nulla, but Fig. No. 3 was taken a few yards upstream from the last exposure of the Murree beds, and shows an asymetrical anticline in the Green shales. Doubtless the thrust continues east of the Khulgai Nulla but is lost in the alluvium and the repetition of Murree sandstones. About the point where the line of thrust would cross the Panoba Nulla, a little above the graveyard, the Murrees show considerable signs of disturbance. It is possible that the large thrust south of Lundaghar (Hill 1475) in the line of the smaller seepage (see Map 1) is the easterly extension of this same fracture.

The Central Thrust.—No signs of over-thrusting is found in either the Khulgai or the Tarkhobi Nullas in the country between the northerly and southerly fractures. In the former nulla the rocks consist of Green shales with an anticlinal structure (see Fig. No. 3); in the latter the Carbonaceous shales outcrop in the stream bed and the Green shales form the low hills in the valley, undoubtedly resting conformably on the former here. In this area they have a very rolling structure. Photo No. 1 is taken in the Carbonaceous shales close to the northerly thrust. Both the Hills 2438 and the horseshoe shaped exposure of the upper limestones on the Maraohagnai Hill consist of a large syncline, in the gypsiferous clays and the Upper limestones on the former hill and of the Upper limestones and the Murrees on the latter hills. Fig. No. 5 shows the synclinal in the Murrees on the latter hill. The difference in the structures of the lower exposures of these hills and the upper series proves that here the succession is not a normal one. Further proof of this is found in the absence of the Nodular limestone on the hill slopes. Between the Green shales and the Upper limestones there must be an overthrust. The hade of this fracture must also be very low to account for both the Khulgai and the Tarkhobi Nullas having cut through the whole of the strata above the thrust plane. Evidence of this thrust and of its low hade is found on the southern limestone slope about one mile west of the Panoba gorge, where two small exposures of gypsiferous clays were found in the line of the thrust

in the Murree beds. Sections Nos. 2 and 3 show the structure at Hill 2438 and Marachagnai Hill respectively. A comparison of these with those of Dr. Pascoe along the same lines (*Mem.G.S.I.*, 40, plate 81) are interesting. The latter do not explain the sudden termination of his Upper limestone band, whereas the former show clearly the unique nature of this occurrence.

Earth Movements.—The earth-movements, that have given rise to the foldings and over-thrusts traced above, undoubtedly had a north and south trend and came from the north. The age of the movement cannot be fixed with any greater precision, than that it was of post-Murree date, as there are no Siwalik rocks in this locality. In other localities, however, it is clear that the movement was post-Siwalik, and must therefore have occurred in post-Tertiary or Pleistocene times. There is evidence, too, that the stresses were continued over a considerable time, as testified by the infoldings of the Murree beds.

Petroleum.

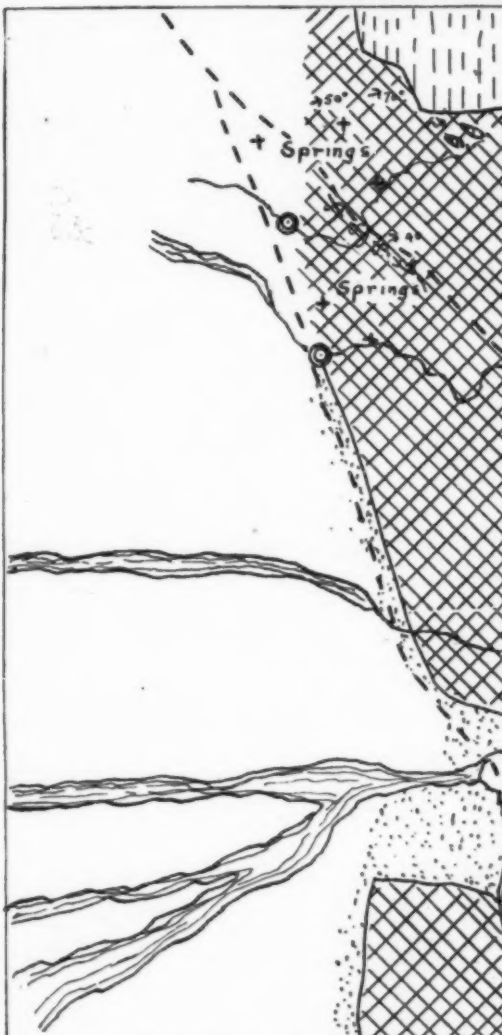
The occurrence of petroleum has long been known here. There are only two seepages, both of which are of very small dimensions.

Panoba Seepage.—The larger of the two is in the Panoba gorge in the stream bed. From the quotation from Griesbach's description, it will be seen that he regarded the oil as issuing from the limestone beds.[60] Pascoe on the other hand writes of an "oil-bearing sandstone" in the gorge.[61] A careful search failed to show any trace of a sandstone. The seepage is undoubtedly from a limestone of the Nodular group; here it has lost its grey colour and is dark brown when freshly broken, due to its oil content. There is little doubt that the oil is however coming from fault planes in the limestone. Griesbach was also of this opinion as he writes: "The oil traces, such as they are, occur in a highly disturbed area, issue actually along lines of fracture and near the northern half of what would have been an anticlinal, if the fault had not lowered the entire Upper Eocene (Murree Series) down to the level of the Nummulitic limestone (*f*), which dips under a high angle to the north."[62]

Later, reasons will be given for the opinion that the true oil horizon is in the basal Nummulitic beds, and that these occur under the Khulgai dome. This oil has migrated along the thrust plane until it has emerged at the surface from the Nodular limestones in the thrust plane, these being the lowest outcrop of porous rock along the fracture. The Nodular limestones, therefore, are

[60] See p. 449.
[61] *Mem G.S.I.*, 40, Pt. 3, 412.
[62] *Rec. G.S.I.*, 25, Pt 2, 106.

—GEOL



—INDEX—

—Scale: ~~1~~ 63,000

Alluvium

Siwalik Gravels

Muree or Kamial

Nummulitic Limestone Upr.

do Gypsiferous Beds do Lowr.

do do Mid.

Pre Nummulitic Beds

Sulphurous Spring

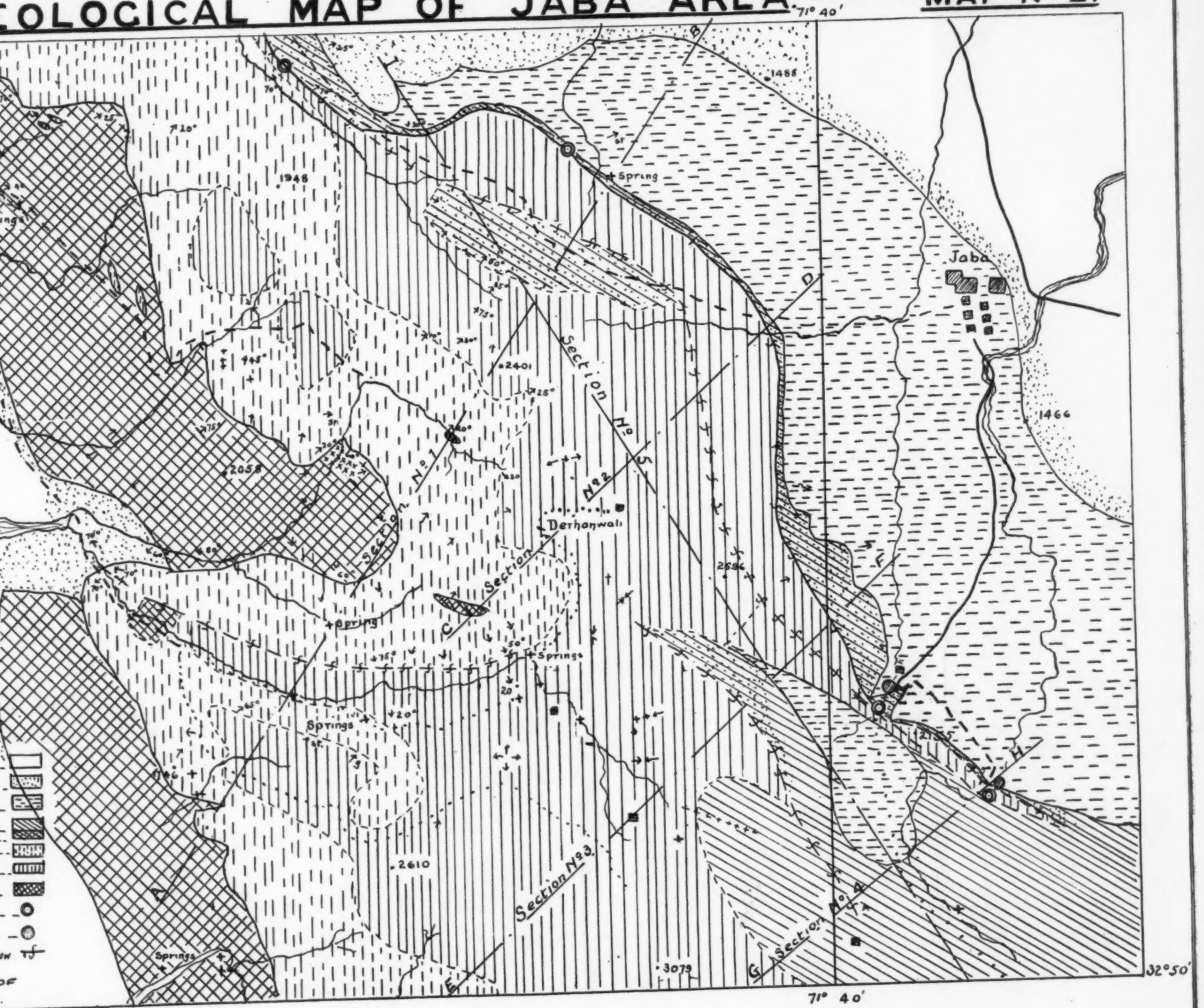
Oil Seepage

Fault, or Thrust. Dash shows downthrow

REDUCED FROM SCALE OF 6 INCHES TO 1 MILE.

32° 30'

...OLOGICAL MAP OF JABA AREA. — MAP Nº 2.



merely a local reservoir rock, and not the true oil zone. This would also explain why there are no seepages in the Tarkhobi and Khulgai valleys as the line of fracture is there in impervious beds.

Eastern Oil Seepage.—The other oil show is extremely small, and occurs in the extreme east of the area mapped, south-east of Hill 1475 (local name Lundaghar). Here is a small watercourse draining into the Indus River. In the headwaters of this stream, the alluvial clays are stained with oil and if disturbed emit a faint odour of petroleum. There is no flow and no emission of gas. An exposure of the gypsum beds is found in the immediate vicinity, and further west there is unmistakable signs of over-thrusting of the Upper Nummulitic limestones on to the Murree beds. It is evident therefore that this oil show too, is in the line of a fracture.

The Jaba Area.

This area is situated at the northern end of the Tredian Hills in the western Salt Range, east of the Indus River. It takes its name from a small village situated at the foot of the eastern slope of the range. The Salt Range here has a northwest to south-east trend, and consists of Carboniferous, Mesozoic, Eocene (Nummulitic), Murree and Siwalik beds. The average height of the range in this part is about two thousand feet above sea-level, but one or two peaks rise to about three thousand feet above sea-level or two thousand to two thousand two hundred feet above the plains. The area has been examined by Mr. Lyman, who reported to the Punjab Government on the oil occurrences about 1870[63]; also by Mr. Wynne, who mapped the entire range for the Geological Survey about 1875-1880[64]; and lastly by Dr. Pascoe in 1913, who mapped the immediate vicinity of the oil springs on the new one-inch maps.[65]

Sequence.—The writer examined the petroleum occurrences in this area, and mapped the area of about twelve square miles shown on Map No. 2. The following rocks were recognised and mapped on the six-inch maps:—

4. Siwaliks.
3. Murree (or Kamlial) Beds.
2. Nummulitic Limestones (Upper, Middle, Lower).
1. Pre-Nummulitics.

Distribution of Strata.

Group 1.—The lowest rocks outcropping in this area are undoubted Carboniferous limestones with crinoids and productus.

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[63] *Rept. on Govt. Oil Lands (Lahore)*, 1870.
[64] *Mem. G.S.I.*, 14.
[65] *Mem. G.S.I.*, 40, Pt. 3, 431-4; plate 87.

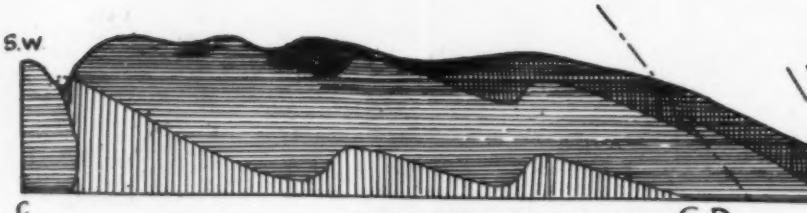
The Triassic series is also represented by green clays and limestones, and it is possible that some Jurassic and Cretaceous rocks may also be present. Wynne has given a very detailed description of a section in these beds a little to the south of this area.[46] No attempt was made to subdivide this group, as they are of no importance in connection with the question of petroleum occurrence, and furthermore everywhere their relations with one another and the younger series were so disturbed, that it was impossible to map them with any certainty even on so large a scale as six inches to the mile.

Group 2.—It will be noticed that the sub-division of the Nummulitic group here differs from that followed in Panoba. It was impossible to recognise the boundaries of the shale groups with any degree of accuracy, as both the black and green shales are much more calcareous, the limestone bands preponderating. That the same general succession applies in the two areas was perfectly clear, but the detailed sub-divisions of Panoba did not lend themselves to mapping in this locality. The limestones above the green shales here are not nodular or concretionary, but such beds here occur at the base of the Nummulitic formation, similar to those found at the base of this formation in the Maidan Range at Mulla Khel. The Nummulitic limestone group was, however, subdivided into three sub-groups: a lower, middle and an upper. The upper boundary of the lower group was placed at the upper limit of the black shaly bands. The middle sub-division consisting of limestones rich in nummulites with thin green shaly partings has a wide extension. The upper boundary of this group was placed at the base of the red and grey gypsum beds, or where these were not clearly developed, where the more sandy type of limestones with large nummulites began to come in. The uppermost subdivision was characterised by sandy limestones with large nummulites, and in some places a development of red and grey gypsum beds. The clear demarcation of this group could not be seen, as in the Panoba locality. In the northern portion of the area the full development of these upper beds is not found, but in the range south of the southernmost oil seepage, and in the synclinal areas north of Sokan, there appears to be the entire sequence of this group, over-laid apparently conformably by the Murree beds.

Group 3.—Pascoe has mapped the red and grey shales and sandstones with dark brown conglomerates as Kamlial (Lower Siwalik), but as I could not distinguish them from the beds mapped as Murree beds in the Panoba area, I have classified them as Murree (or Kamlial) beds. They appear to be conformable to the upper

[46] *Mem. G.S.I.*, 14, 259-263.

SECT



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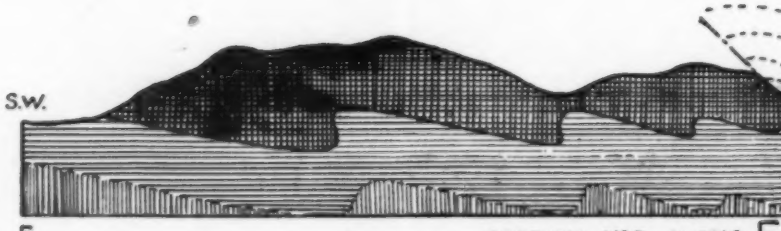

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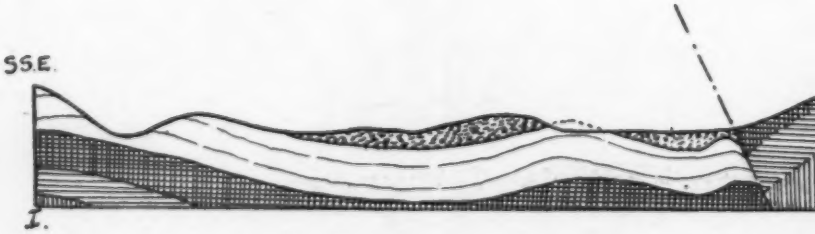


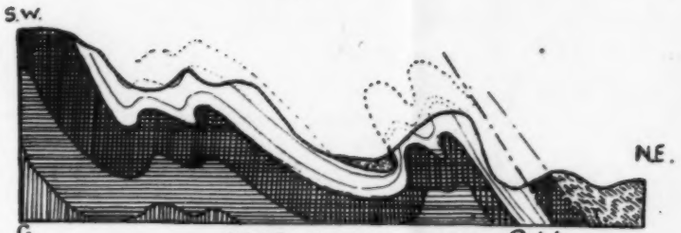
MAP 2 (SECTIONS).

JABA AREA.

—·—·— = Thrust plane.

SECTION No 1 ALONG A.B

C.D.



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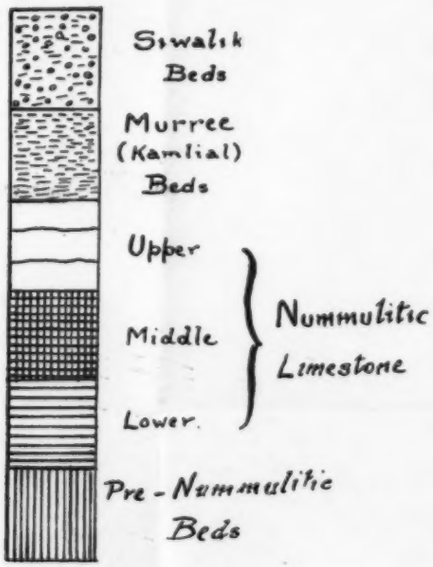
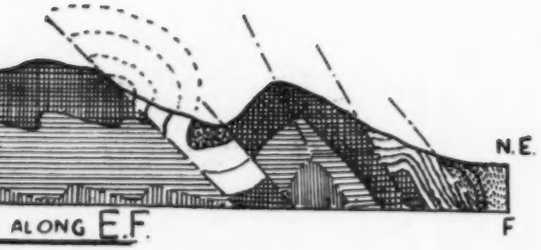
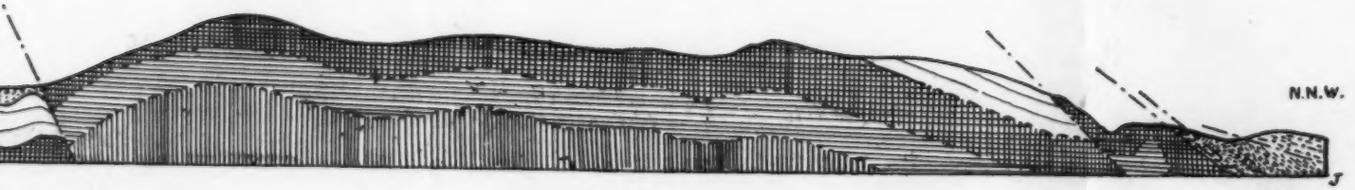




ALONG E.F.

SECTION No 5 ALONG I.J.



Nummulitic group in the synclinal areas north of Sokan, in which case they would be Murree beds. This point, however, requires more detailed examination, especially as basal Murree (or Kamlial) beds in the northern portion of the area mapped contain pebbles of limestones undoubtedly derived from Upper Nummulitic beds, and thus indicating at least a local unconformity. The beds of this series consist of red and purple clays intercalated with greenish sandstones and some dark brown conglomerates. The latter rock is described by Wynne as a "pseudo-conglomerate."[67] They have a limited outcrop, only occurring along a strip of country forming the eastern boundary of the Nummulitic limestone country and in two small synclinal areas. In the former outcrop, they are over-thrust upon the limestone beds. In the extreme north-east of this area they are cut out by Siwalik beds, which have been thrust over them and brought into contact with the grey gypsiferous clays of the Nummulitic group. The beds have here an isoclinal structure and dip steeply to the east and north-east.

Group 4.—Undoubted grey sandstones with some shales occur in the east of the mapped country and are of Siwalik age. Pascoe maps their junction with the Murree (or Kamlial) beds as a normal one, but the detailed mapping has proved that it is an uncomformable one, most probably due to over-thrust. The over-thrust nature of the junction of these beds and the gypsiferous beds in the extreme north-east is indisputable. These beds have a general easterly or north-easterly dip, at lesser angles than the underlying Murree (or Kamlial) beds. In the Katha Nulla further east they are almost horizontal.

Further, some coarse brown conglomerates are exposed to the south of Khairabad in the west of the area mapped. These beds have been mapped as Siwalik, but it is possible that they are of post-Tertiary age, and equivalents of the similar beds found at Nammal and Kalabagh, though they are disturbed having a westerly dip.

Comparison of Present and Previous Maps.—It will be found that there are several important differences between the present map and that published by Dr. Pascoe on the one inch to the mile scale.[68] These are particularly noticeable along the eastern boundary of the Nummulitic limestone outcrop, where the boundary of the Murree (or Kamlial) and the Nummulitic beds is further east on his map. Again the synclinal area north of Sokan village is shown by Pascoe as extending northwards over the divide into the valley west of the oil seepages. This is not so, the divide

[67] *Mem. G.S.I.*, 14, 265.
[68] *Mem. G.S.I.*, 40, Pt. 3, plate 87.

here consisting of Upper Nummulitic limestones, and the synclinal areas being separate. Again in the extreme north-east the S_2 group of Dr. Pascoe is in direct contact with the gypsiferous beds of the Nummulitic division north-east of Hill 1184, having been over-thrust completely over the Murree (or Kamlial) beds. In the present map the Nummulitic limestones have been sub-divided into a lower, middle and upper group.

Structure.

An examination of Pascoe's map shows that he does not recognise any thrusting or faulting, but stipulates an anticlinal and synclinal structure disturbed by minor faults. Pinfold, who also examined the area regards the structure as a monoclinal one. He writes: "At its western end the Salt Range turns abruptly northwards into the Indus valley, and along the eastern side of this arm the uppermost bed of the limestone contains native sulphur and oil. It is a chalky limestone similar and probably the equivalent of the passage beds (*i.e.*, Lower Chharat) of the northern sections. The largest seepage is at Jaba and this locality has yielded small quantities of oil for many years. The structure is monoclinal, the limestones dipping steeply beneath the upper Tertiary sandstones and shales."[69]

Evidences of Over-Thrusts.—The detailed mapping has shown that the structure is not so simple as either of the above-mentioned workers indicate. For example, on the cliff face south-east of Khairabad a number of Nummulitic limestone outcrops occur amongst the Mesozoic strata there exposed. Their position cannot be explained by any system of folding, and they have undoubtedly been over-thrust into these positions. Again, south of the large Mesozoic outcrop, members of the middle group of Nummulitic limestones are found underlying the lower group, and a line of over-thrust can be traced a distance of about two miles.[70] Another over-thrust was traced about half a mile to the west of the oil springs, where a synclinal containing Murrees and the Upper limestones are thrust upon the middle and Upper group. In the nulla bed a little upstream from the more southerly seepage, an overfold in the upper limestones can be traced northwards into an over-thrust bringing these beds first in contact with the Murree beds and yet further northwards bringing the middle sub-division in contact with the Murree beds.[71] The entire eastern boundary of the Nummulitic group is an indisputable

[69] *J. Proc. Asiatic Soc. Bengal* (*N.S.*), 1918, **14**, clxxix.
[70] See Map. 2 (section 1).
[71] See Map 2 (section No. 3).

over-thrust, and the line of fracture is almost everywhere occupied by the red or grey gypsiferous beds. In some places they are very thin, and in others have a considerable thickness and show a highly folded structure. They are absent to the south of the most southerly seepage. The sulphur and the sulphuretted hydrogen emissions are from these beds and not from the limestones as stated by Pinfold above. The anticline in the limestone beds east of the northern seepage is a highly faulted one,[72] and the oil is issuing from the limestone beds in this faulted zone, and not from the gypsiferous beds. Unfortunately the author's photographic evidences from this area did not come out successfully, as the negatives were spoilt by the climate.

This area lies in one of the regions where the Salt Range undergoes one of the changes of direction, which is so marked a feature of the range. South of the most southerly oil spring, the thrust has been from the north. North of the seepages however the movement was from the east. In the general considerations drawn from this detailed work it will be suggested that this area lies in the region of a "Tear Plane."[73] The Nummulitic strata have been folded into marked anticlines and synclines prior to the fracturing which is more extensively developed here than at Panoba. The highly fractured structure here developed is undoubtedly due to the presence of the underlying Paleozoic and Mesozoic strata, and the crumpling against these of the newer unconsolidated strata. The newer strata have finally glided over this local horst, thus accounting for the varied direction of some of the thrusts.

Petroleum.

Oil has been known to occur here for very many years, and about 1905 two wells were drilled in the stream bed near the northern oil spring. Both these began in the gypsiferous beds in the thrust zone, and both were dry holes. One was taken to about 300 and the other to about 500 feet. Some months after the work was abandoned, oil appeared in the more westerly bore hole and has continued to flow very slowly ever since. The Military Works Department have obtained about one thousand gallons yearly from this source, and used it for a lighting plant at Rawalpindi. There is little doubt that the oil has found its way through the broken ground in the thrust plane to the oil well. The fact that the holes were dry is explained by the impervious nature of this rock. The source of the oil is undoubtedly in the broken anticline

[72] See Map 2 (section No. 3).
[73] See p. 485

to the west of the seepage, and the oil zone is most probably the basal nummulitic beds, as at Panoba, and similarly un-exposed under the anticline in the limestones.

The following is an analysis of the oil at present flowing in the well:—

Analyses of Jaba Oil.—(Prepared by Mr. Briggs, Analytical Chemist, Calcutta.)

Specific gravity at 15·5° C.		0·9310
Flash-point (Pensky-Marten's) closed		116° C.
" " open		126° C.
Viscosity (Redwood) at 100° F.		3′ 40″ (220 secs.)
" " at 140° F.		1′ 25″ (85 ")
Free fatty acid as oleic acid		0·60
Saponification value		7·3
Saponifiable fatty oil		3·7%
Mineral acid		nil
Fractional distillation:—		
Below 220° C.	nil	Benzene, naphtha
220°—300° C.	25%	Burning oil (kerosene)
300°—360° C.	62%	Lubricating oil
	6%	Tar, etc.
	7%	Coke

Asphaltic Base.

The absence of volatile constituents is most probably due to the fact that the oil has migrated a considerable distance and collected in the well very slowly, the lower volatiles passing off, and the oil becoming somewhat inspissated. A remarkable feature is that the oil is reported to have an asphaltic base, whereas Attock oils are reported to have a paraffin base. Dr. Pascoe also reports that samples from this area supplied to Messrs. Price & Co. in 1857 were favourably reported upon for candle making, though later bulk samples were spoken of as unfavourable.[74]

The Kundal Area.

The remaining area mapped on the six-inch scale is that comprising the northern end of the Khasor Range in the trans-Indus Salt Range, immediately south of the village of Kundal at the junction of the Rivers Indus and Kurram. The area covers about 12 square miles and is bounded on the east by the Indus River and on the west by the Paniala Nulla. About 1875 Mr. Wynne mapped this on the scale of one-inch equals one mile,[75] and in 1913 Dr. Pascoe re-mapped a portion of it, having now the advantage of the new one inch to the mile maps published by the Topographical Survey of India.[76]

[74] *Mem. G.S.I.*, 40, Pt. 3, 433.
[75] *Mem. G.S.I.*, 17, Pt. 2.
[76] *Mem. G.S.I.*, 40, Pt. 3, plate 86.

The writer examined the petroleum occurrences in this neighbourhood in 1923-4, and in order to arrive at an appreciation of the economic possibilities of the occurrences mapped the area on the scale of six inches equals one mile. The following sequence was recognised and mapped:—

Grey sandstone series	Siwalik
Red and drab clays	Murree (Kamlial)
Conglomerates	Do.
Nummulitic limestones	Eocene (Nummulitic)
Sandstones (with oil) and clays with carbonaceous matter)	Eocene (Nummulitic)
Thinly bedded limestones, clays and sandstones	Mesozoic (Trias to Cret.(?)
Massive limestones	Carboniferous or Permo-Carb.

This was the same grouping that had been recognised and mapped by Dr. Pascoe.

Sequence.—In his earlier mapping, Wynne had not recognised any Nummulitic limestones. He records some magnesian limestone, the age of which puzzled him, but he finally grouped them with the older rocks, as he found them resting on the Carboniferous limestone. He also records "Salt Marls or Saline series" in the area south of Ram Kund and these he regarded as the equivalent of the same beds in the Salt Range and mapped them as Silurian (?).[77] These gypsiferous beds are included by the writer in the Mesozoic. At the time he mapped this area he was unfamiliar with the gypsiferous beds of Nummulitic age, and therefore grouped them with the rocks in which they occurred. It is exceedingly probable, however, that these beds are the equivalents of the Lower Chharat red and gypsiferous marls, seen in both Panoba and Jaba, and that they owe their position here to having been squeezed along the thrust plane.

Distribution of the Strata.

Carboniferous.—The Carboniferous limestones are well exposed south and south-west of Domniwala. A crinoidal limestone also of this age occurs south of Ram Kund. The beds are extremely massive crystalline limestones similar to those of the Pennine Range. They are the oldest rocks seen, but are found resting on newer strata in two or three cases.[78] They form the crest of the range at the Siana Vanda where they rest on the Mesozoic (Triassic) beds.

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[77] *Mem. G.S.I.*, 17, Pt. 2, 58-60.
[78] See Map 3 and sections Nos. 1-3.

Mesozoic.—On the eastern flank of the range (Hill 1650) above Ram Kund are exposed some thinly bedded limestones with shales and coarse pebbly sandstones and flags.[79] In these Wynne has found Ceratites, establishing a Triassic age for the beds. Associated with them are some white and red mottled sandstones similar to rocks which in other localities are classified as of Jurassic age. Wynne's remarks on this group are worthy of repetition:[80]

"This part of the section on the shattered side of the outcrop is more or less obscure and repetitions of the beds may occur; but superficial subsidence of the rocks will not entirely account for the presence of a group of white, red and mottled sandstones and clays and magnesian limestone layers having exactly the appearance of the variegated portion of the Jurassic group. I suppose these to represent some sub-carboniferous rocks brought into this position by faults; unless indeed the group be altogether a new one intermediate between the Carboniferous and the Trias. These are the rocks doubtless referred by Fleming to the Salt Group of the Salt Range and by Verchere to the same horizon called by him 'Saliferian.'"

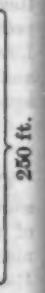
"In a deep kas between Ram Kund and Duman-wali hamlet or kiri I found these beds dipping west at 35° apparently overlying the Ceratite Beds without discordance of any kind, which nevertheless might be present."

(Section after Wynne.)

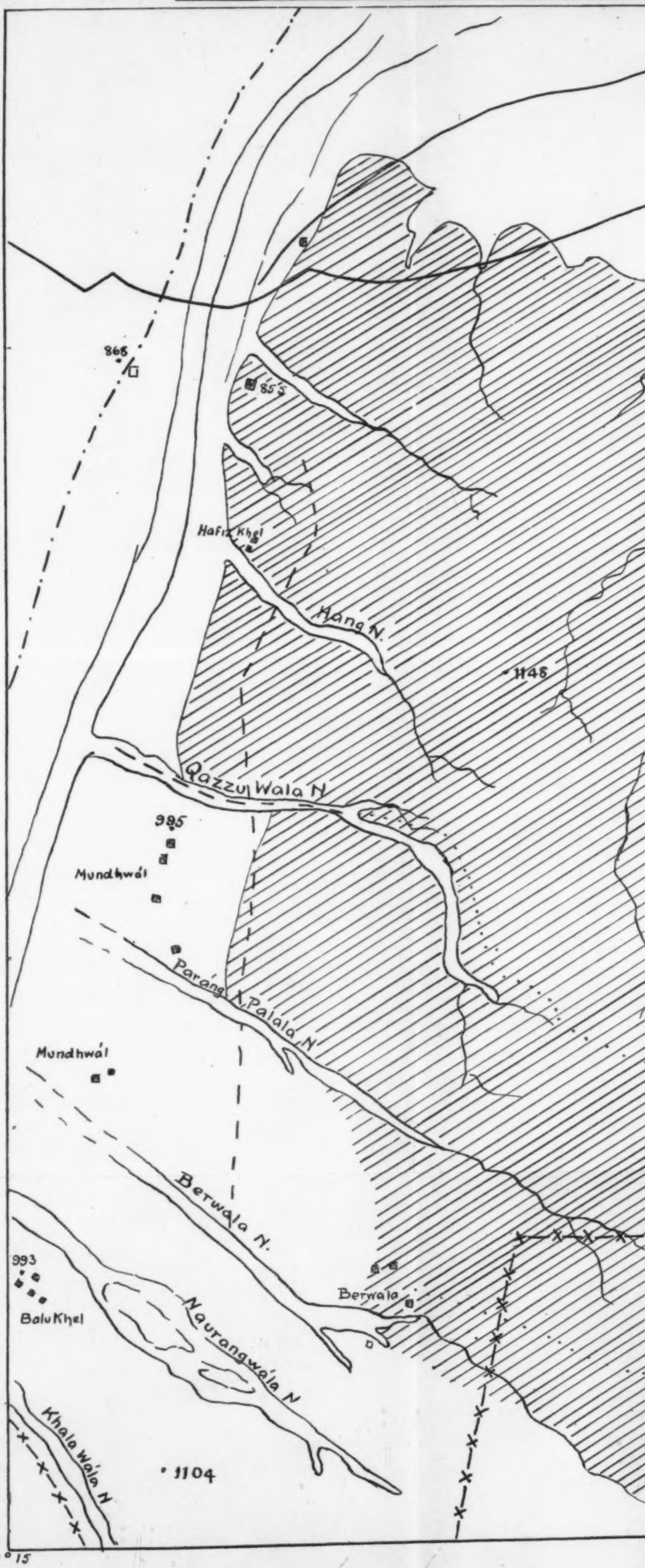
Ceratite flags, flaggy limestones and marls more than 30 ft.	
Thick reddish purple clays with small strings of a white fibrous mineral soft like gypsum and slightly saline	250 ft.
Mottled purple and white sandstones	
Coarse gravelly white sandstones	
Variegated pink lavender white and greenish clays and white sandstone	
White soft sandy rock (rotten)	
A few bands of white earthy limestone (magnesian) with white and green clay partings	
White sands and decomposed sandstone (once calcareous or magnesian)	
Variegated purple and green grey clays	

In spite of the above remarks he shows these beds on his maps as the "Salt Marls" of Silurian (?) age. Pascoe says of these:—

[79] See Fig. 15. Trias over-thrust on Carboniferous.
[80] *Mem. G.S.I.*, 17, Pt. 2, 58.


250 ft.

GEOLOGICAL MAP



OF KUNDAL — MAP No 3.

Attock Paniala

720

Kundal

Sahibdad Shahwala

Ziarat

Mian Malúk Ali

Ram Kund

1650

Domni Wala

659

1300

Siana Banda

Jhugge

Siani Vanda ▲2268

71°20'

INDEX

Scale 2½ inches to 1 mile

- Alluvium
- Chinji Beds
- Kamial Beds
- Kamial Conglomerate
- Nummulitic Limestone
- Oil Series
- Mesozoic Rocks
- Carboniferous Limestone
- Oil Show
- Igneous Intrusion

REDUCED FROM SCALE OF 6 INCHES TO 1 MILE

"My own opinion is that they are of Mesozoic age occurring normally between the Carboniferous and Tertiary, the upper boundary being unfaulted."[81]

This is, however, not sufficient, as it does not explain how in the one case they rest on Carboniferous and in the other on Triassic rocks. My maps and sections[82] will show that this area is cut up by numerous thrust planes, and this supports the suggestion given on page 469, that the red and gypsiferous beds are the Lower Chharat beds squeezed in along thrust planes in which Triassic Jurassic and Carboniferous strata have been caught up, as we have seen is so in a much less degree at Panoba and Jaba.

An igneous rock occurring in the Triassic series a little upstream in the Algad from the oil-seepages should be mentioned. This is the only igneous rock in the area and is a green trap rock intrusive into the Triassic limestones and clays. It is identical with the extrusive rock seen at Mulla Khel (see page 444).

Eocene.—The following detailed description of the section at one of the oil seepages by Wynne cannot be improved upon[83]:—

Siwalik (?)	10. Red and drab clays with pebbly and other soft sandstones of grey colour	500 ft.
	9. Thick conglomerates with irregular sandy layers at base	15–20 ft.
Upper part of Ceratite Group (?)	8. Brown limestone with white carbonate of lime geodes	5 ft.
	7. Sandstone layer	1 ft.
	6. Brown calcareous sandstone, joint spaces filled with calcareous mudstone	10 ft.
	5. Greyish pink shale with calcareous sandy layers	3 ft.
	4. Brown slightly calcareous layer saturated with tar	7 ft.
	3. Soft greyish white sandstone	100 ft.
Ceratite Beds	2. Shaly variegated pink and purple grey olive flaggy beds with brown fossiliferous limestone layer with Ceratites	50 ft.
	1. Hard thin limestone with Ceratites	(?)

It will be noticed that Wynne puts them with certain reservation into the Triassic group. In this connection, he writes[84]:—

"It is difficult to fix the age of the middle rocks in the last section, such limestone as occurs here intercalated or entangled with the lowest tertiary conglomerate might be found in the Trias, Cretaceous (?) or Eocene (?) it contains no fossils and the presence of petroleum rather adds to the difficulty. The usual place of this

[81] *Mem. G.S.I.*, **40**, Pt. 3, 425.
[82] See Map 3 and sections.
[83] *Mem. G.S.I.*, **17**, Pt. 2, 60.
[84] *Mem. G.S.I.*, **17**, Pt. 2, 61.

being near the top of the Eocene limestones, which are altogether absent here. In no place is such a limestone or any limestone known to form layers in the Siwalik beds, so the presumption is that the calcareous beds are here older and that its fretted shore surface was so filled by the material of the conglomerate, that where the sandy layers of the latter meet others of the limestone the distinction becomes effaced. The thick soft sandstone too (No. 3) being so far as I could see unfossiliferous is not easy to refer to any fixed horizon; it is not seen to occupy its place for any considerable distance and though bearing a certain amount of resemblance to the sandstone on the supra Jurassic horizon, it may just as possibly belong to either of the next underlying groups. Below it the rocks are a part of the Ceratite group and as the black belemnite zone does not occur beneath the sandstone it may for the present be left with the group on which it rests."

An examination of the section at Mulla Khel in the Maidan Range showed a limestone, which was similar to that exposed in this region, and which there appeared to be undisturbed with reference to the Nummulitic limestone group. Associated with the limestone there is a series of sandstone and shales with coal seams. A similar group of rocks occurs in the western Salt Range at Nammal. These basal beds have been described on pages 443 and 444. Hence there is no doubt that the sequence that Wynne had such difficulty in placing should be classified with this group. They are therefore basal Nummulitic beds, and their relation to the underlying Ceratite (Triassic) beds is due to over-thrusting. Fig. No. 16 shows a wisp of these sandstones caught up in the red and drab clays which both Pascoe and Wynne agree are of Siwalik age. It will be seen from the following that Pascoe is also of opinion that these oil beds here should be included with the Nummulitic group:—[85]

'Above these beds (*i.e.*, the Mesozoics) near the oil seepage come alternating laminæ of dark shales and thin micaceous flags followed by two or three bands of hard grey limestone containing no fossils and weathering brown. Then come 40 ft. of alternating sandstone and clay bands over which considerable quantities of tar have trickled, followed by some 50 ft. of massive light coloured to medium to fine textured calcareous sandstone from which oil oozes. The last bed is elsewhere more of the nature of a limestone, and as far as can be made out is the Magnesian limestone of Wynnes' fig. 6, p. 268. Whether any of the above beds are Cretaceous is not known, but I see no reason why the oil horizon should not be accepted as Nummulitic. They appear to be above beds resembling

[85] *Mem. G.S.I.*, **40**, Pt. 3, 426.

the Jurassic and are unconformably overlain by a conglomerate belonging to either the Murree or to the Siwaliks."

It should be here stated that Pascoe did not recognise the over-thrust nature of the Siwalik and older rocks junction in this algad, but explained it as due to an extensive overlap of the Siwaliks on to the older beds here.[86]

Nummulitic Limestone.—Wynne did not recognise any Nummulitic limestones in this region and none are shown on his map.[87] Pascoe on the other hand mapped the limestones forming the summit of Hill 1650 as Nummulitic.[88] It has been shown above that similar limestones occur above a similar sandstone bed with coal at Nammal and Mulla Khel, so there is no doubt that these beds should be classified with the Nummulitic group. In this area there is only a small development of these limestones and only the very basal members are present. Every exposure is in an over-thrust position and it is clear that no complete sequence of beds of this age occurs. The maximum thickness cannot exceed 200 ft. It is a massive cherty more or less magnesian limestone and everywhere unfossiliferous. It weathers similar to the Hill limestone of other areas. It rests on all the groups here exposed except the Siwaliks.

Murree (or Kamlial) Beds.—Wynne and Pascoe both refer the red and drab clays and conglomerates exposed in the Basti Algad to the Kamlial group of the Siwaliks. In the text, however, the latter shows uncertainty on this point by referring to them as the "Murree or Kamlial" group (see quotation above). Owing to the similarity of these beds with others in the Kohat district, which are there mapped as "Murrees," the writer has preferred to leave this an open question. That these beds are over-thrust upon various groups in this locality is clear from the field sections (see also map and sections) Pascoe explains the varying contacts as due to extensive overlapping of these beds, but the detailed mapping shows that this is not so.[89]

Conglomerates.—The conglomerates usually occur at the base of the above clays, but in a number of places are over-thrust on to older beds. It is possible that some of the conglomerates included in this group may be of post-Tertiary age and the equivalent of those found at Nammal and Kalabagh, the disturbed character of this country however renders it impossible to decide.

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[86] *Mem. G.S.I.*, **40**, Pt. 3, 428.
[87] *Mem. G.S.I.*, **17**, Pt. 2, plate 1.
[88] *Mem. G.S.I.*, **40**, Pt. 3, plate 87.
[89] See also Fig. No. 16.

Structure.

Pascoe describes the structure of this area in the following words:—[90]

"The structure is that of an anticline disturbed on both flanks. There is the usual over-folding towards the east but in addition there has been under-thrusting in the western limb, producing a subsidiary fold on this side. The subsidiary fold in the section through Siana Vanda is of the nature of an inverted syncline, but near the oil seepage it becomes a parasitic anticline over-folded towards the east like the parent syncline (see Section Plate 85). At Siana Vanda the Carboniferous limestone strikes approximately north and south and is overlain uncomformably by the Kamlials (or Murrees). One and a half miles north of the peak the limestone outcrop leaves its north and south strike and swings quickly round to the east, indicating an abrupt pitch northwards. At the same time new beds rapidly appear between it and the Tertiary ferruginous sandstone. This is a case of rapid unconformable over-lap."

It is clear from the above that Pascoe regards the salient features of the area to be due to over-folding but no over-thrusts, and recognised the varied junctions as due to extensive over-lap of the Tertiary beds.

Wynne on the other hand recognised that there had been considerable earth-movement and shattering of the rocks together with displacement, and possibly repetition, but was evidently at a loss to explain the associations.[91] He appeared to favour a structure of isoclinal folds dipping steeply to the west, and such faults as he did map, he regarded them as normal faults. The map and the sections[92] on the scale of six inches to the mile show clearly that no system of folding could explain the distribution and associations of the various rock groups. The sections of Dr. Pascoe referred to in the above quotation afford no explanation of the absence of the S_1 and S_2 groups on the eastern side of the range; nor do they explain how the Carboniferous beds come to rest on the Mesozoics east of Siana Banda.[93] The outcrops of the Tertiary conglomerates and limestones, and the lenticles of Jurassic sandstones on the eastern face of the rage cannot possibly be fitted in with any system of over-folding, and can only be the result of over-thrusting. Wynne's figure (p. 60, *M.G.S.I.*, vol. 17, pt. 2) becomes perfectly clear if it be recognised that over-thrusting has taken place.

[90] *Mem. G.S.I.*, **40**, Pt. 3, 427.
[91] *Mem. G.S.I.*, **17**, 58.
[92] See Map 3 and sections. (Reduced in scale.)
[93] *Mem. G.S.I.*, **40**, Pt. 3, plate 85.

The rocks have an isoclinal structure, dipping to the west and north-west. They have been subjected to great lateral pressure from the west, and this tectonic force has folded the newer rocks against a core of Carboniferous rocks now exposed in the vicinity of Domniwala. The pressure has been so intense, and the rocks have fractured and been over-thrust to such a degree, that all signs of the original folds have been lost.

There is abundant evidence in the field of such over-thrusting. Fig. No. 15 taken in the large right bank tributary of the Algad, W.S.W. of Hill 1857 shows the Triassic beds crumpled and over-thrust upon the Carboniferous limestones. In the extreme left of the photograph, the red and drab clays of Siwalik age are overthrust upon the Trias. These are the T_3 and T_2 thrust planes of sections Nos. 1 to 3 (Map sections 3). The pinching out of the Trias between these two thrusts is well exposed north-west of Siana Banda.

Another striking example of over-thrusting occurs in the second right bank tributary of the Algad from its mouth. The rough sketch plan and vertical section Nos. 5 and 6 (see Map sections 3) show this occurrence. It could not be decided whether the limestones exposed near the junction with the main stream are of Carboniferous or Nummulitic age; but it is clear that there are numerous over-thrusts here bringing in wisps of Tertiary sandstones, clays, and limestones and probably even Carboniferous limestones in inextricable confusion.

Photograph No. 16 is an ocular demonstration of the over-thrusting that has taken place. This shows a lenticle of the oil sandstone of Basal Eocene age in the red and drab clays of Siwalik age at No. 7 Seepage. In the small left bank tributary of the Algad near its mouth, a lenticle of red and drab clays in the Siwalik (Chinji) sandstones is exposed, and has been caught up in the latter beds, which have been thrust upon the main out-crop of the former in the Algad. In the second left bank tributary from its mouth, a dark brown conglomerate band has been repeated by over-thrusting no less than three times in a section of about 200 yards across the strike of the beds. On the east side of the range the thrusts cannot be traced so clearly, as along the Algad, as this being the scarp face, the structure is hidden by talus. North-west of Ram Kund the cutting off of the Mesozoics is well exposed in the stream. The thrust was here from the north-west and this junction is undoubtedly a "Tear Plane," the Nummulitic limestone to the north having been carried much further to the south-east. The lenticular patches of red and white sandstones (mapped as Mesozoic) which Wynne[94] recognised were similar to

[94] *Mem. G.S.I.*, 17, Pt. 2, 58.

the Jurassic sandstones of other localities, are doubtless wisps caught up in the thrust planes. South of Ram Kund crinoidal Carboniferous limestones are resting upon Mesozoics. Again near Siana Banda the productus limestone rests on Mesozoic limestone and yet further north the same bed is found in contact with Nummulitic limestones. We have seen on pp. 469-471 that along this face gypsiferous beds of doubtful age occur, sometimes resting on Triassic and sometimes on Carboniferous beds in apparent conformity. The knowledge we have gained at other localities has led us to regard these as members of the Lower Chharat group squeezed in along thrust planes.

We are unable to interpret the sequence of earth-movements here with the precision with which we followed them at either Panoba or Jaba; but it is probable that the Carboniferous limestone formed a horst against which the over-lying beds were crumpled and over-thrust. A very complex system of folding was produced, and as at Panoba, shearing and over-thrusting of these folds took place. Thus is explained the varied contacts of strata met. The mapping work has proved at least six thrust planes and the curious sequence of beds on the eastern face of the range can only be explained by the thrusts having cut across the tops of anticlinal crests and carried forward at the base of the thrusts wisps or lenticles of the Mesozoic and Carboniferous strata of the cores.

Thrust Planes.—On the western slope of the range several thrust planes can be followed considerable distances. The thrust T_1 of sections 1-3 (Map sections 3) is well exposed in the left bank tributary near the mouth of the Algad, where it brings the Siwalik (Chinji) beds on to the red and drab clays of Lower Siwalik age. In the extreme south of the area mapped, this thrust has transgressed so far eastwards that it has cut out all the Lower Tertiaries and Mesozoics and has brought the Chinji sandstones in conjunction with the Carboniferous limestone. The thrust plane T_2 of sections 1-3 (Map sections 3) can be traced from the mouth of the Algad almost continuously to the southern limit of the area mapped. As followed from north to south it cuts across the sequence and brings almost all the members of the rock groups in contact with one another.

The thrust T_3 of sections Nos. 2 and 3 (Map sections 3) can be followed at least two miles. Fig. No. 15 shows this thrust plane very clearly, the Trias being crumpled and carried forward on to the Carboniferous beds. It also shows the T_2 thrust which brings the red and drab clays of Siwalik age on to the Mesozoics. Every outcrop of oil rock and every seepage is either along the T_2 or T_3 thrust planes or in the country rock caught up between these two thrusts.

The thrust T_4 of section No. 2 (Map sections 3) can be traced at least a mile from north of Siana Banda to Hill 1857. This thrust, though it is probably the oldest of the area, is of relatively recent age as proved by the intrusive rocks in the Mesozoic beds on both sides of the thrust. We have seen on p. 444 that these igneous rocks were intruded in Cretaceous and probably late Cretaceous times. It is impossible to correlate the numerous thrusts in the eastern portion of the area. In the country east of the large oil sandstone exposures, the rocks are extensively fractured, and it is exceedingly probable that this marks a region of "Tear Planes." These "Tear Planes" no doubt are due to the fact that the resistance offered to the over-riding Tertiaries and Mesozoics was less in the north, where the Carboniferous core has a "pitching anticlinal structure."[95] West and south-west of Domniwala the thrusts are from the west, but to the North-west the direction of over-thrusting was from the north-west. This like the development of the "Tear Planes" was due to the pitching of the Carboniferous core. The final movement was undoubtedly the pushing forward of the Siwalik beds from the west, and this has proceeded so far that it has cut out all the Lower Tertiaries and Mesozoics, except at the northern end of the range. It is clearly a case of over-thrusting and not over-lap as regarded by Dr. Pascoe.[96]

An examination of Map 3 shows that the strike of the Siwalik Series follows a wavy line from north to south. In the extreme north-west, the strike is almost due east and west, and as traced southwards towards the oil seepages gradually swings until it is a little west of north and east of south. Further south it swings back to due north and south. These alterations of strike, or rather the forces which gave rise to them, have caused the older rocks to fracture, but the newer and less consolidated deposits bent rather than broke, and consequently show a marked swinging of the strike.

Petroleum.

There are no less than seven oil seepages in the area mapped, and they all occur along the line of the Algad, which as above indicated follows the line of a large thrust plane (see Map 3). The oil seepages are shown on the map by patched circles. In all cases except one the oil shows occur in the sandstone rock of Basal Eocene age, here mapped as the "Oil Sandstone." The exception occurs from a conglomerate, which at that place overlies

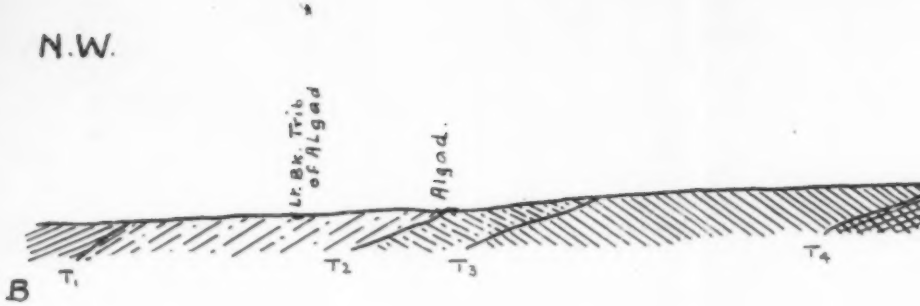
[95] *Mem. G.S.I.*, **40**, Pt. 3, 427.
[96] *Mem. G.S.I.*, **40**, Pt. 3, 428.

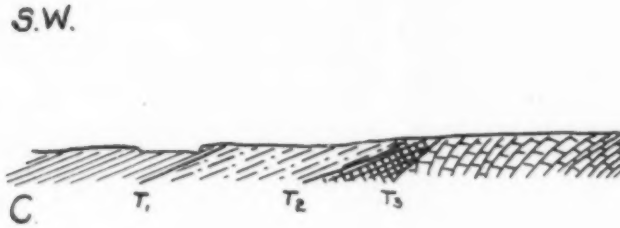
the oil sandstone. None of the shows are accompanied with any show of gas. It will be seen that all the oil seepages occur at or near the western limit of the exposure of the oil rock, which supports the view that such seepages are merely the drainage from the sandstone to the rise of the show. With the exception of Seepage No. 7 the oil indication is at a point where the Tertiary groups show a change of strike. Two borings were made in the bed of the Algad a little west of Oil Seepage No. 2, and although in the shallow depths small shows of oil were met, no yield of any importance was obtained, and the borings ceased at 640 and 390 feet respectively. The structure in the beds here is unfavourable to any economic yield, and indeed, it is very uncertain to what extent the oil strata may continue to the dip. It is very probable that these beds are cut off by further thrusts in that direction.

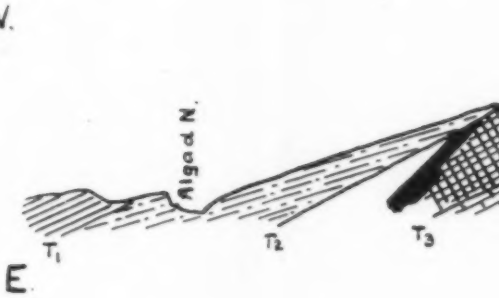
General Considerations.

General Application of Results.—Having studied in detail the relations of the various groups of rocks and the structure developed in them in the particular areas examined, we can now attempt to bring this knowledge to bear on the geological problems yet remaining unsolved, or in doubt, in the Salt Range its trans-Indus extension and the Kohat Hills. The literature written on these problems is extensive and abounds in differences of opinions and theories of solution. These difficulties and the various theories offered as explanations have been admirably reviewed and summarised by Dr. Pascoe.[97] As he rightly remarks "the questions will probably not be settled until the Salt Range is remapped on a scale larger than that possible to Wynne."[98] Dr. Pascoe makes out a very strong case for the theory which "assigns all the salt (both of the Salt Range and Kohat) to the Eocene period and makes that of the Salt Range over-thrust by the Paleozoic."[99] We have seen in the areas mapped, that such over-thrustings as Dr. Pascoe stipulated on theoretical grounds must have taken place, have played an important part in the distribution of the various rock groups. We have further seen that in the Kohat Hills the development of asymetrical anticlines and their over-thrusting is markedly developed; and we have been able to trace this development with great precision. In the western Salt Range at Jaba a similar type of folding and over-thrusting has been elucidated, but here it has been of such intensity that it was impossible to trace the definite folds and their development into

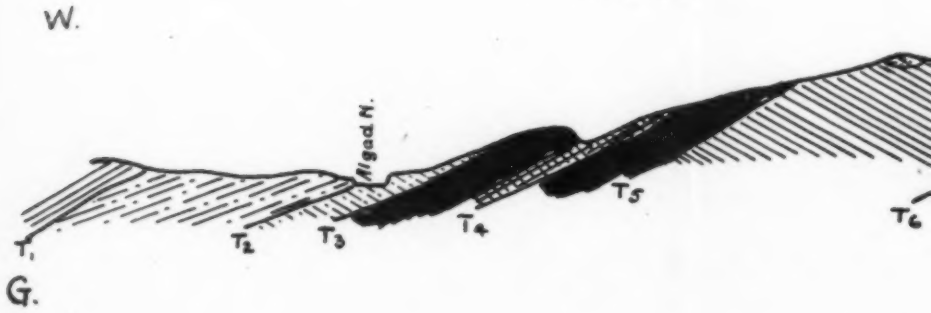
[97] *Mem. G.S.I.*, **40**, Pt. 3, 352-70.
[98] *Mem. G.S.I.*, **40**, Pt. 3, p. 352.
[99] *Mem. G.S.I.*, **40**, Pt. 3, 363.







SECTION NO. 4 ALONG GH.
Scales as No. 3.



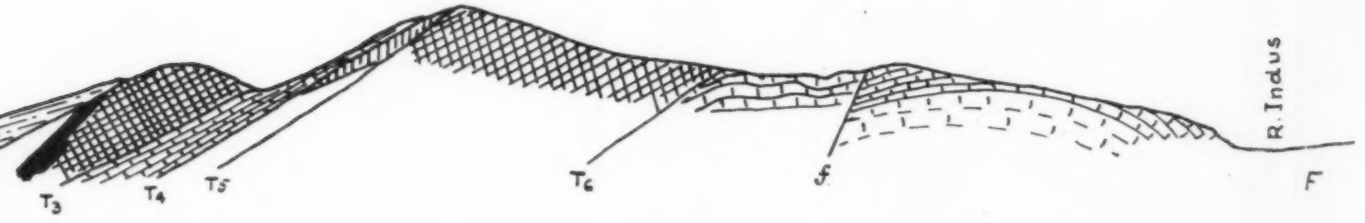
MAP 3 (SECTIONS).

KUNDAL AREA.

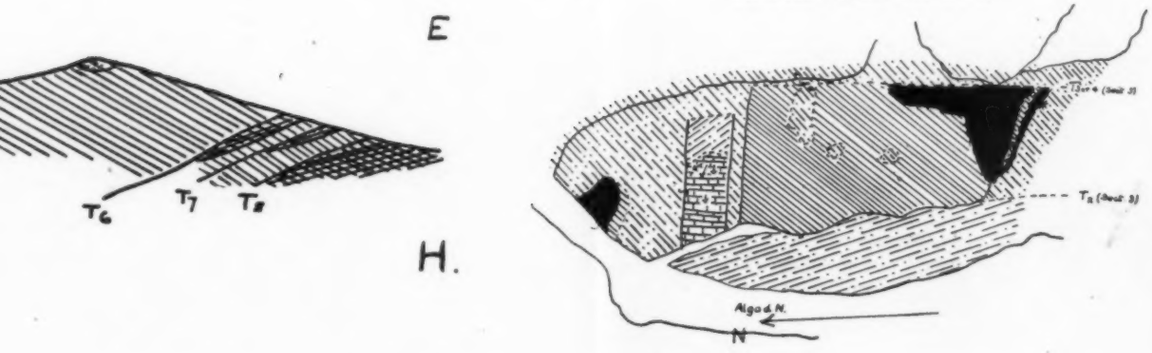
SECTION NO. 1 ALONG AB.
Scale: Horizontal and vertical 6 in. = 1 mile.

SECTION NO. 2 ALONG CD.
Scale as above.

SECTION NO. 3 ALONG EF.
Scale: Horizontal 6 in. = 1 mile; vertical 1 in. = 1000 ft.



NO. 5.—ROUGH SKETCH PLAN AT POINT Z (SEE APPENDIX B).
Not to scale. Approx. 12 in. = 1 mile.



NO. 6.—VERTICAL SECTION EXPOSED AT *NO. 5.
Not to scale.

over-thrusts except in one or two cases. These folds and thrusts have here produced a great entanglement of the various groups present. In the trans-Indus extension in the Khasor Range, the same movement has been seen, but the rocks are in such inextricable confusion that the individuality of the folds has been lost in the bewildering heterogenity of the stratigraphical relationships produced.

Difficulties to be Solved.—It is clear from the analysis made by Dr. Pascoe and referred to in the foregoing paragraph, that the chief difficulties remaining to be solved are :—

1. The age or ages of the Salt, Salt Marls and associated rocks of the Salt Range and the Kohat Hills.
2. The relation of the Purple Sandstone to the Salt Marls.
3. The mode of deposition or origin of the Salt Marls.

And in addition to these, it is hoped the present work will throw some light on the further questions :—

4. The tectonics and structures of these hills.
5. The relation of these ranges to the Himalayan and Hindu Kush Mountain systems.
6. The important part played by the Salt Marls in deciding the tectonic structures, which the earth-movements have imparted to the rocks of this area.
7. The idigenous horizon of the petroleum deposits scattered throughout this region.

Age of the Salt Marls, etc.—The Salt Marls are a curious deposit, which have long excited the interest of geologists and given rise to considerable differences of opinion regarding their origin and place in the geological sequence. Wynne grouped these together with the Salt, Gypsum, and the Purple Sandstone as the " Saline Series " a name first used for them by Dr. Fleming. Early workers in this area had classified them as Devonian,[100] Permian,[101] Trias,[102] Eocene,[103] and intrusive.[104] It will be realised, therefore, that the field relations of the group must be very varied and the difficulties of placing it very real. Wynne finally assigned these beds of the Salt Range and its trans-Indus extension to the early Paleozoic and older than the " Obolus Beds " which overlie them at Kheura.[105] Subsequently the " Obolus Beds " yielded Hyolithes and trilobites and have been definitely assigned to the Cambrian group.[106]

[100] *J. Proc. Asiatic Soc. Bengal*, **18**, 661.
[101] *J. Proc. Asiatic Soc. Bengal*, **23**, 651.
[102] *J. Proc. Asiatic Soc. Bengal*, **35**, **36**, Pts. 2.
[103] *Proc. Geol. Soc. London*, **7**.
[104] *J. Proc. Asiatic Soc. Bengal*, **17**, 500. *Rec. G.S.I.*, **24**, 26-42.
[105] *Mem. G.S.I.*, **14**, 73.
[106] *Rec. G.S.I.*, **27**.

According to Wynne therefore the "Saline Series" are of pre-Cambrian age. It is evident from his descriptions of these rocks that Wynne was very puzzled regarding their age, and as Pascoe says, "was forced to his conclusion somewhat against his instinctive judgment."[107] If it be conceded that over-thrusting has taken place in the Salt Range, the fact of the "Obolus Beds" overlying the "Saline Series" loses its significance and we are compelled to look elsewhere for the true position of the latter in the geological sequence.

Pascoe has emphasised the improbability of either :—[108]

1. There being two salt zones, one of pre-Cambrian age and the other of Eocene age, within twenty miles of each other; or

2. The preservation of a pre-Cambrian salt in Kohat "through such a vast period of time, *i.e.*, early Paleozoic to early Tertiary."

His difficulty in assigning the salt of both the Kohat and the Salt Range to the pre-Cambrian era was "to explain the complete absence of the Paleozoic and Mesozoic in a section which has a still greater appearance of a normal, conformable, undisturbed sequence in Kohat, where also we have salt at the base and a Nummulitic limestone at the top." The difficulty in placing the salt in the Eocene group was to explain "the regular series of beds from Cambrian to Nummulitic lying in proper sequence above Salt Marl, Gypsum and Purple Sandstone in the Salt Range."

Dr. Murray Stuart tells the writer that a few miles north of Nilawan, the whole of the strata between the Saline Series and the Nummulitic limestone, which is given in Wynne's description of the section at Nilawan,[109] is cut out and the Nummulitic limestone is found resting on the Salt Marl. Pascoe[110] also states the salt "shows contortions in excess over that which the superposed rocks have been subjected.' This is exactly what we have found in the gypsum beds along the southern thrust at Panoba (see Fig. No. 4). Both these are evidence that over-thrusting has occurred in the Salt Range. Diagrams 2A and 2B taken from Wynne's and Middlemiss's work are further evidence of such over-thrusting. It follows, therefore, that there is no difficulty in assigning the salt of both areas to the Eocene, as it may be taken as proved that the sequence in the Salt Range is not a regular one but disturbed by over-thrusting.

It has been demonstrated in the foregoing pages that the degree of folding and over-thrusting is much less in Kohat than in the

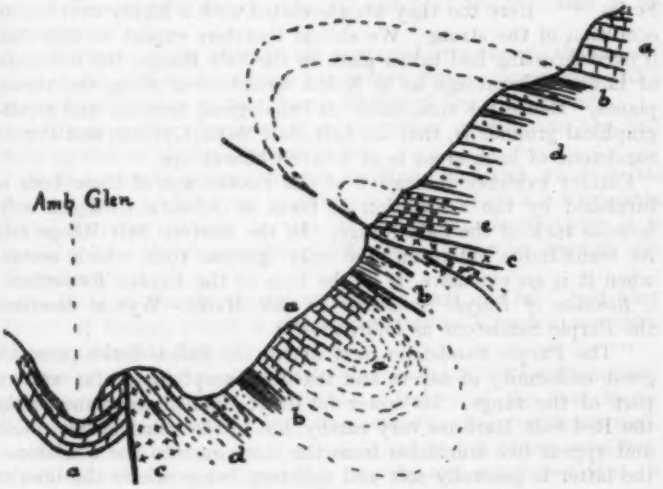
[107] *Mem. G.S.I.*, **40**, Pt. 3, 358.
[108] *Mem. G.S.I.*, **40**, Pt. 3, 358-9.
[109] *Mem. G.S.I.*, **14**, 190.
[110] *Mem. G.S.I.*, **40**, Pt. 3, 355.

Salt Range or its trans-Indus extension; a fact also recognised by Pascoe, vide the quotation above. On a priori grounds, therefore, we should turn to the former area in any endeavour to arrive at the normal sequence of the strata.

fig 26 Section West of Dandôt
(after Wynne)
Mem. G.S.I vol XIV p. 162

A.

a.—Purple S.S. b.—Redder S.S. c.—Gypsum band. d.—Olive S.S. e.—Coal shales. f.—Nummulitic Limestone.



B.

SECTION AT AMB GLEN.
(After Middlemiss, *Rec. G.S.I.*, Vol. 24, Pt. 1.)

c.—Gypsum band. e.—Boulder bed. d.—Speckled S.S. b.—Lavender beds. a.—Productus Limestone.

DIAGRAM 2.

We have seen that the succession at Panoba in the Lower Chharat stage is gypsiferous grey clays below with red clays above; but there is no salt present. Pascoe however describes the salt of Kohat as associated with grey gypsiferous clays.[111] Griesbach[112] in the Narai Sar section of the Safed Koh Range found a purple sandstone in conformable sequence above the red clays. At Jatta, east of Banda Daud Shah, the salt is associated with the red clays. At Bahadur Khel similar clays occur with the salt. Wynne himself recognised the Eocene age of the salt and salt marls of the Kohat area.[113] At Panoba the soft red plastic gypsiferous clays have thickened and thinned according to their position in the folds and occur squeezed from regions of high to those of low compression, and along almost every thrust plane. At Jaba this was not so clearly evident, but still the significance of the occurrence of these beds in the thrust planes could be realised. At Kundal the beds were not recognised, but subsequent knowledge leads us to think that the gypsiferous beds mapped with the Mesozoics should be referred to the Lower Chharat. This supposition is also supported by the fact that both Fleming and Wynne have mapped them as the equivalents of the "Saline Series."[114] Here too they are associated with a highly over-thrust condition of the strata. We should therefore expect to find that if over-thrusting had taken place in the Salt Range, the red clays of Lower Chharat age as in Kohat would occur along the thrust planes. Hence the conclusion on lithological, tectonic and stratigraphical grounds is, that the Salt, Salt Marls, Gypsum and Purple Sandstone of both areas is of Lower Chharat age.

Further evidence indicative of the Eocene age of these beds is furnished by the association of them at Kheura with the only igneous rock of the Salt Range. In the western Salt Range and its trans-Indus extension, the only igneous rock which occurs, when it is an extrusive, is at the base of the Eocene formation.

Relation of Purple Sandstone to Salt Marls.—Wynne describes the Purple Sandstone as follows:—[115]

"The Purple Sandstone next above the Saline Series possesses great uniformity of aspect and texture, except in the far western part of the range. Its lower 50-100 ft. immediately succeeding the Red Salt Marl are very earthy, but of the usual purple colour and appear like transition from the marl up into the sandstone; the latter is generally soft and splintery below where the lines of

[111] *Mem. G.S.I.*, **40**, Pt. 3, 355.
[112] *Rec. G.S.I.*, **25**, Pt. 2, 102-3.
[113] *Mem. G.S.I.*, **11**.
[114] *Mem. G.S.I.*, **17**, Pt. 2. *J. Proc. Asiatic Soc. Bengal*, **22**.
[115] *Mem. G.S.I.*, **14**, 84.

bedding are not very clearly marked. Above the earthy portion, argillaceous inter-stratifications are rare or absent and the beds are all of a nearly equal hardness, considerably less than that which is usual in Paleozoic rocks."

Middlemiss, on the other hand, denies that these beds pass gradually into the marls and cites a number of cases refuting the above.[116] These exceptions are undoubtedly explicable on the grounds of over-thrusting, and Middlemiss's sections support this conclusion. Griesbach has shown that similar Purple Sandstones occur above the Red Marls in the Lower Chharat stage at Narai Sar.[117] This Kohat area is the least disturbed area in which these rocks are found, and it is reasonable to assume that the normal order is therefore here present, and that in those cases where the sequence differs, such difference is due to earth-movement. Indeed, many of the cases cited by Middlemiss in support of his intrusive theory of origin of the marls, give evidence of the sandstone being normally above the marls. It is therefore reasonable to assign these beds to the Eocene group and to see in them the equivalents of those rocks at Narai Sar.[118] Dr. Pascoe while not dogmatising on this point ventured the opinion that these beds are of Eocene age (Lower Chharat) and gave the following as his reasons :—

(*a*) In spite of the effect of the supposed over-thrust, the greater part of the Purple Sandstone has a very young appearance and a strong resemblance to the Purple Shales of the Chharat age.

(*b*) It is highly ferruginous, a character common to the salt marl as well as to the Chharat beds.

(*c*) It is closely associated with the Red Marl with which it has in some places a brecciated junction, and with which it is frequently folded up ; in contrast to this its upper boundary, where it is overlain by Cambrian beds is described as abrupt, though not discordant.

(*d*) Beds of Purple Sandstone form a part of the "Red Clay Zone" of Kohat, which is almost certainly of Upper Nummulitic (Lower Chharat) age.

Mode of Origin of the Red Marls.—As early as 1853, Dr. Fleming[119] called attention to the remarkable character of the Red Marls. In some localities it has the characteristics of an intruded rock, while in others it appears brecciated, and in yet others stratified. Middlemiss[120] also examined this deposit and concluded that it

[116] *Rec. G.S.I.*, **24**, 31.
[117] *Rec. G.S.I.*, **25**, Pt. 2, 102-3.
[118] *Mem. G.S.I.*, **40**, Pt. 3, 355, 363.
[119] *J. Proc. Asiatic Soc. Bengal*, **17**, 500 *et seq.*
[120] *Rec. G.S.I.*, **24**, 42.

was not a sediment, but suggested its being something "of the nature of a scum, such as we might picture to ourselves as having been partly secreted at the surface of an ancient untapped magma." He recognised that the "intrusive or injective impetus (of the substance) followed by consolidation" took place during the Tertiary period.[121] Dr. Christie explains that this intrusive appearance may be due to its plasticity and does not necessarily indicate an igneous origin, nor does it necessitate the conclusion that it is of a later date than its position simulates.[122]

It is clear, therefore, that opinion is divided, as to whether this deposit is of sedimentary or of intrusive origin. In the Kohat district, no doubt whatsoever is held as to the sedimentary character of the gypsiferous red marls, it being agreed that it was deposited in a gulf in a region of dessication.[123] If we agree that the red marls of the Salt Range are of identical age with those of Kohat, we must of necessity adopt the same theory of origin for both. It is difficult to imagine such rocks as products of igneous activity, as they show no definite flow structure, no crystallisation, and no such igneous product is known elsewhere. There is, however, no necessity to have resort to such an unprecedented mode of occurrence, if we realise that each of the peculiarities noted can be explained by considering the results which would arise from the squeezing of a highly plastic gypsiferous clay along lines of thrust. In the eastern Salt Range, Middlemiss has proved similar occurrences of this deposit in the cores of flexures and along lines of fracture, just as we have found in the Jaba and Panoba areas.[124] Indeed, our work has provided an explanation not only of its origin, but also of the varied characteristics it is found to assume.

Tectonics and Structures.—We have seen that in the areas mapped on the large scale, the general structure is due to extensive folding, the development of reversed folds and over-thrusts. It is significant that in his explanation of the structures at Kalabagh and Nundrakki, and to account on theoretical grounds for the absence of the Saline beds in the sequence above the plain, Dr. Pascoe stipulates that reverse folding and over-thrusting must have taken place, though he failed to recognise it in his mapping of the Panoba area.[125] In the latter area, as the folds and over-thrusts have only exposed the Tertiary strata, we can trace the developments very clearly, and have been able to trace

[121] *Rec. G.S.I.*, **24**, 42.
[122] *Rec. G.S.I.*, **44**, 261.
[123] *Mem. G.S.I.*, **40**, Pt. 3, 455-7.
[124] *Rec. G.S.I.*, **24**, 33.
[125] *Mem. G.S.I.*, **40**, Pt. 3, 363-370.

the transgression of the thrusts across the strata. In the Jaba and Kundal areas where Mesozoics and Paleozoics have been caught up in the thrusts and exposed, there is greater difficulty in tracing the local development of the structures. Sir Thomas Holland was, I believe, the first to suggest that the numerous difficulties in connection with the geology of the Salt Range might be explicable by the aid of over-thrusting, such as we have proved.[126]

If we examine Wynne's geological maps of the Salt Range and its trans-Indus extension in the light of the knowledge gained in the particular localities examined, we see that every occurrence of the Saline Series shown on these maps is explicable on the theory of over-thrusting.[127] Especial attention is called to the deposits of Salt Marl in the Lunai Nulla north of Kalabagh, where their presence is undoubtedly due to their having been squeezed in along a "Tear Plane," which has carried the Siwaliks, etc., southwards to form the western portion of the Salt Range. The line of fault marking this "Tear Plane" is clearly shown in the local map prepared by Wynne.[128] Similar "Tear Planes" would appear to occur a little north of west of Sakesar; between Vasnal and Dheri in the Central Salt Range; and again in the line of the Diljaba Mountains and a little east of Dilwat (N. of Dandot).

The importance of the reversed fold in the structure of the Safed Koh Range was recognised by Griesbach[129] and Hayden.[130] The latter writing on the structure of the hills south of the Safed Koh Range says:—

"The rocks of this area appear at first sight to dip steadily at low angles to the north, but on close inspection are found to be thrown into a series of folds, frequently reversed. . . . . The key to the structure of the whole area is, however, the inverted fold, and when examined in this light the whole of the section from the Khyber to the Samana resolves itself broadly into a series of inverted folds, often much complicated by crumpling and faulting, the faults frequently taking the form of over-thrusts."

Incidentally, too, it may be pointed out that Dr. Hayden found representatives of the Carboniferous, Trias, Rhaetic, Cretaceous and Jurassic rocks evidently included in these folds much as we have found at Jaba and Kundal.

If further support for the statement, that this reversed folding is typical of the structure of the Salt Range, its trans-Indus extension, and the Kohat Hills, be required, the reader is referred to

[126] *Imp. Gaz.*, **1**, ii., p. 22.
[127] *Mem. G.S.I.*, **14**; **17**, Pt. 2.
[128] *Mem. G.S.I.*, **17**, Pt. 2, 44.
[129] *Rec. G.S.I.*, **25**, Pt. 2, 105.
[130] *Mem. G.S.I.*, **28**, 97.

the numerous descriptions and sections by Wynne,[131] Middlemiss[132] and Stuart.[133] The latter has found that in the salt beds there is evidence of over-thrusting, and explained the pollution of the salt with bitumen, oil and gas by migration of the oil along these thrust planes.[134]

Relation of these Hills to the Himalayan and Hindu Kush Systems.—With reference to the relation of this group of hills (the Salt Range, its trans-Indus extension and the hills of Kohat) to the Himalayan and Hindu Kush systems of mountains foldings, the following remarks from Dr. Oldham's are of special interest in view of the type of folding we have proved common to the structures here :—[135]

"In his great book, 'Das Antlitz der Erde,' Prof. Suess has regarded the Salt Range of the Punjab as forming part of the foot-hills of the Hindu Kush and has united all the ranges between it and what is known to geographers as Hindu Kush, into one range, on the ground that they belong to the Hindu Kush system of disturbance. This is still a matter for proof. . . .

"As regards the Salt Range we shall shortly see that it ought to be classed by itself, and the undoubted individuality of the Safed Koh Range as depicted on our maps is so marked, that it is difficult to believe that it has not also an individuality of structure. . . . The hills (*i.e.*, Salt Range) are composed of a plateau with steeply scarped face to the south along which there is an axis of abrupt faulting accompanied by more or less faulting. . . ."

Again Wadia writing on the subject of the Mountain Ranges of India says :—[136]

"The Salt Range must be held as an illustration of a dislocation mountain. Its orthoclinal outline, *i.e.*, its steep southern scarp and the long gentle northern slope, suggests that these mountains are the result of a monoclinal uplift combined with vertical dislocation along their southern border, which has depressed the other beds underneath the plains of India."

Griesbach in his paper on the Safed Koh Range says :—[137]

"Considered therefore from either purely geographical, structural or casual point of view I contend that the Salt Range with the north-west Punjab hill ranges belong rather to the Himalayan

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[131] *Mem. G.S.I.*, **10**, **14**; **17**, Pt. 2.
[132] *Rec. G.S.I.*, **24**.
[133] *Rec. G.S.I.*, **50**, 1, 4.
[134] *Rec. G.S.I.*, **40**, Pt. 4.
[135] *Man. of Geol.* (*Oldham*), pp. 7-9.
[136] *Geol. of India* (*Wadia*), p. 275.
[137] *Rec. G.S.I.*, **25**, Pt. 2, 66.

area of elevation than to that of the Hindu Kush, with which it does not seem to have any other connection than the more or less doubtful similarity of strike."

Not Dislocation Mountains.—It is clear from the above quotations that there are three distinct opinions regarding the classification of these hill ranges. Dr. Oldham and Dr. Wadia evidently look upon the Salt Range and its associated hills as "dislocation mountains" not directly connected with any mountain building system, but due to *vertical uplift* and monoclinal folding.

We have seen in the last few pages that the reversed folding with over-thrusting is the typical structure of the areas in these hill systems. Surely such structures are more associated with "lateral," than "vertical" uplift. We shall see later that it has also many similar features to the Himalayan System and, indeed, structures can be traced from one Himalayan mountain area into these hills. We can, therefore, at once conclude that this area if not related to the Himalayan Mountain system is certainly not a "dislocation mountain."

Prof. Suess places these hills in the Hindu Kush system of mountain folding, while Griesbach, who did a considerable amount of field work in the Himalayan, North-west Indian and adjoining areas, states they have nothing in common to that system.

Similarity to Hazara (Himalayan) Structures.—Medlicott[138] and Middlemiss[139] working in the Himalayan ranges have proved that there the typical structure is the reversed fold. The latter writer has examined the Hazara District which adjoins this area to the north-east. A study of his map[140] and the map prepared by Dr. Pascoe[141] showing the petroleum occurrence is very instructive. The "Main Boundary Fault" of Middlemiss can be traced westwards into the area under consideration and the Panoba area is seen to be on its extension to the west. The system of over-thrusting we have traced in this latter area would therefore appear to be the westward extension of Middlemiss's "Main Boundary Fault" in the Hazara District. A comparison of the types of folding we have traced in the Panoba area with those proved by Middlemiss in the Hazara District shows a remarkable similarity. Middlemiss himself recognised the extension of his principal Hazara "Himalayan features" to the west, and indeed traced the westward extension of his "Nummulitic and Upper Tertiary Zones with all Characteristics."[142]

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[138] *Mem. G.S.I.*, **3**.
[139] *Mem. G.S.I.*, **24, 26**.
[140] *Mem. G.S.I.*, **26**, Map. Also *Geol. of India* (*Wadia*), fig. plate 19.
[141] *Mem. G.S.I.*, **40**, Pt. 3, plate 70.
[142] *Mem. G.S.I.*, **26**, 269.

Middlemiss's remarks in this connection are important and deserve repetition. Writing on the system with which the Hazara foldings should be placed he says :—[143]

"The sharp bend of the strike of the strata at the Jhelum and in the general run of the rocks and mountain ranges from a N.W.–S.E. or W.N.W.–E.S.E. to S.W.–N.E. or W.S.W.–E.N.E. following respectively the trend of the Himalayan on the one hand and the Hindu Kush on the other, has been considered as a proof that here are indicated two systems of earth-movements distinct in origin and perhaps in age. . . .

"On a small scale as in the Salt Range, we know how flexures of the rocks perfectly parallel for considerable distances will sometimes suddenly veer for a while through as much as a right angle. A change of direction therefore, even a sudden one in the trend of the axis of lines of disturbance need not always imply distinctness in origin and age. . . . Petrologically and structurally the Himalaya and the countries west of the Jhelum R are the same."

Our work has proved that the structures of the Salt Ranges, its trans-Indus extension, and the Kohat Hills, where examined are of the "Himalayan" type, and therefore we can support Griesbach in his assertion that these hills should be classified with the Himalayan Mountain Building System. Wynne evidently attributed the origin of these ranges "to the mountain building movements that formed the Western Himalayas, the Suleiman and the Afghan Ranges."[144]

This question is perhaps worthy of a little more detailed study. Middlemiss has shown that the characteristic of the "Sub-Himalayan Zone" is the development of what Medlicott named "Boundary Faults."[145] That Middlemiss recognised the similarity between the break south of the Salt Range and the "Himalayan Boundary Fault" is clear from his remarks.

"*Boundary Faults.*"—The principal characteristics of the "Himalayan Boundary Faults" are :—[146]

"1. Their parallelism to the General strike of the adjacent formations; a fact which marks them as being of the nature of fold faults or highly dipping thrust planes.

"2. Their characters as being lines dividing one zone from another; thereby indicating how the extra elevation and compression of each zone found relief by the packing up of the strata and by sliding over its neighbouring zone to the south-east."

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[143] *Mem. G.S.I.*, **26**, 282-4.
[144] *Mem. G.S.I.*, **17**, Pt. 2, 18-19.
[145] *Mem. G.S.I.*, **24**, **26**.
[146] *Mem. G.S.I.*, **26**, 265-6.

Often these "Boundary Faults" approximately mark the limit of deposition of the beds in contact with the fault on its south side, though in the case of the "Nummulitic Boundary Fault" Middlemiss recognised that that could not be regarded as a limit of deposition of the Nummulitic limestone in the Hazara District.[147] The thrusts in the Salt Range, the Kohat Hills and the trans-Indus Ranges show the two characteristics tabulated above; though like the "Nummulitic Boundary Fault" they are not limits of deposition of any definite strata. For example, Wynne shows Siwaliks both north and south of thrust at Chichali Pass west of Kalabagh. Again Murrees outcrop both north and south of the Thrusts at Panoba; and according to Wynne's map Siwaliks outcrop south of the eastern Salt Range near Jalalpur.

In the Himalayan area, Middlemiss has shown that the "Boundary Faults" are not "contemporaneous but successional," and claims that the most southerly are later than those to the north.[148] In the region now under consideration we can trace many "thrusts," but as they do not limit the deposition of any group of strata, we have not the guage wherewith to measure the times of the movements, as is found in the eastern districts. For the same reason in this locality we cannot term them "Boundary Faults." There is no doubt that these thrusts were formed in the same way as the "Boundary Faults," *i.e.*, by a fracture developing in an over-fold as depicted in Sketch No. 8 (Map sections 1). As in the case of the "Boundary Faults" the thrusts here were not contemporaneous. The earth-movement affecting this area were undoubtedly progressive and the thrusts merely mark the breaking point of the strata, when the crumpling and folding had progressed to such a degree that the inverted or reversed folds gave way and a portion of the fold slipped over the recumbent limb, largely, as we shall see shortly, due to the consistency of the red marls intercalated in the folded strata.

Earth-Movements.—The earth-movements which have affected this region may be divided into two categories, though latterly they were doubtless stages of the same movement:—

(*a*) Relatively gentle oscillations raising and lowering the area above or below sea-level.

(*b*) The great plicating mountain building movement.

Hayden[149] has traced the various uplifts and depressions, which have effected this area since Cambrian times, and has shown that from Carboniferous times onwards this area was in close proximity to the Gondwana Continental Shore line. Pascoe has followed

[147] *Mem. G.S.I.*, **26**, 277.
[148] *Mem. G.S.I.*, **26**, 267.
[149] Burrard and Hayden, Calcutta, 1908, pp. 250-7.

in great detail the Cretaceous-Eocene movements and shown how they gave rise to gulf conditions in this locality.[150] We have seen that in Basal Eocene (Basal Nummulitic) times portions of this area was a land surface. Nuttall has proved the same oscillations in Lower Lakki times in the Sind area.[151] The lithological study of the Nummulitic rocks shows that this was a period of oscillation and that up to this time at least, the mountain building movement had not resulted in excessive folding and uplift here.

Middlemiss in his paper on the Hazara District states:—[152]

"It is only when the Himalayan area is left and we pass on to the Salt Range, the Suleman Range and the hills of Sind, that we find marine strata of greater thickness and encroaching somewhat higher into the Tertiary Series. A fact which indicates that the wave of elevation took place from the east to the west, whereby the sea-level was driven in that direction and estuarine and fluviatile conditions supervened."

Griesbach[153] in his article on the Safed Koh Range points out that in the Perso-Afghan watershed, marine conditions continued into late Miocene times and possibly Pliocene, which supports the east to west wave of elevation stated above. The same writer also points out that in the Salt Range the principal disturbances took place after the deposition of the Nummulitic formations.

It will be concluded therefore that the later oscillations in this region, *i.e.*, those in Cretaceous and Eocene times, were connected with the mountain building movements, which later (in post-Tertiary times) subjected the strata here to intense plication. Prof. J. K. L. Martin, of Leyden University, in his paleontological work in the Dutch East Indies,[154] and particularly in connection with his work on the fauna of the Nangoellan Series of Southern Java, has proved that about Oligocene times the uplift of the area to the south of the Tethys Sea had progressed so far, that the connection of this sea with the Pacific, which had existed probably between India and Madagascar,[155] had been closed. This mountain building movement caused waves of elevation from east to west and the wave had not advanced sufficiently far in the region of the Salt Range to cause acute folding and fracture until post-Siwalik times. The troughs of Nummulitic-

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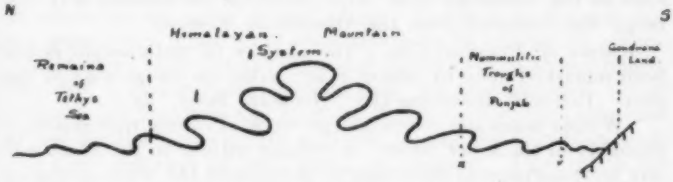
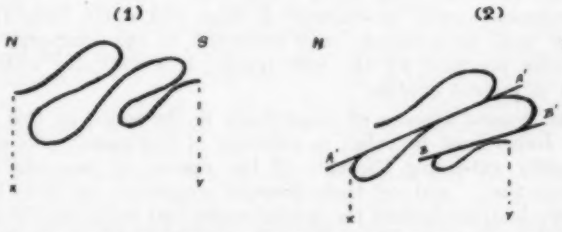
[150] *Mem. G.S.I.*, **40**, Pt. 3, 450 *et seq.*
[151] *Quart. J. Geol. Soc.*, **81**, Pt. 3, 426 *et seq.*
[152] *Mem. G.S.I.*, **24**, 113.
[153] *Rec. G.S.I.*, **25**, Pt. 2, 66.
[154] *Samml. Geol. R. Mus. Leiden*, 1914, **9**, 357-55.
[155] Hayden and Burrard, pp. 249-258.

Murree age traced by Dr. Pascoe in the north-west Indian area,[156] were undoubtedly formed in the synclinorum to the south of the Himalayan folding. This folding movement subsequently transgressed over this very region, and gave rise to the reversed folds and over-thrusts, we have traced in our detailed work.

The Diagrams Nos. 3A and 3B will explain how this mountain building movement affected the region now under consideration. No. 3A shows the great fan fold which produced the main Himalayan-Thibetan Ranges and the synclinorum depression



A.—DIAGRAMMATIC REPRESENTATION OF HIMALAYAN FOLDING IN NUMMULITIC TIMES.



B.—DIAGRAMMATIC REPRESENTATION OF LATER FOLDING OF NUMMULITIC TROUGH AREA XY AND DEVELOPMENT OF OVERTHRUSTS.
A'A'.—Nummulitic Boundary Fault. B'B'.—Main Boundary Fault.

DIAGRAM 3.

which gave rise to the gulf conditions of Nummulitic times. Further folding raised this area above the sea-level in Murree times, and subjected the rocks of the "Nummulitic Trough Area" to over-folding and ultimately to over-thrusting as shown diagrammatically in Sketch No. 3B. Undoubtedly the geographical conditions in this area in Nummulitic times were comparable to those at present prevailing in the Maracaibo and North Venezuelan shores. Portions

[156] *Mem. G.S.I.*, **40**, Pt. 3, 451-3.

of the shore line were fretted with lagoons with a rich flora and plant life, while in other parts arms of the sea were cut off from the main ocean and salt deposited under the arid climatic conditions. The absence of salt deposits over large areas in both the Salt Range and the Kohat Hills is an indication that the salt was deposited in separate basins, and not in one large continuous sea. Indeed the formation of isolated lagoons would be expected under the uplift due to these folding movements. The apparent isoclinal dip of the rocks of the Salt Range with the steep scarp slope to the south; the absence of any sign of dynamic metamorphism even in the Cambrian beds, were doubtless the reasons why this range was excluded from the Himalayan System.

Absence of Metamorphism.—The absence of metamorphism has been remarked upon by almost every writer on the geology of this area. Pascoe[157] describing the "Neobolus Beds" says:—

"Wynne notes the occasional presence of strong ripplemarks—probably in the lower layers—a striking witness to the absence of any metamorphosing disturbances throughout the whole geological record."

Wynne says:—[158]

"What the conditions were, which thus confined the deposits of a geological system so extensive in time with so few indications of even local unconformity and restricted to the comparatively small area occupied by the Salt Range, is a difficulty which I cannot at present explain. . . .

"The general absence of discordance in the series on this side of the Indus must be taken as evidence of enormously prolonged tranquility extending through all the epochs of paleozoic and cainozoic time; and yet these tranquil conditions can have been but very local for besides the unconformity just mentioned beyond the Indus, there is the most palpable discordance at Sirban Mountain in the Himalayan Region between the infra-Triassic beds and *the underlying slates supposed to be Silurian—a formation of which the Salt Range representative is perfectly conformable with the rest of the series.*"[159] (See also the quotation on p. 442.)

The work of detailed mapping has brought out the important role that the gypsiferous beds have played in the determination of the structures developed. We have seen that these beds are responsible for the curious shaped folds found.[160] Is not the unaltered, unmetamorphosed state of the deposits in this region

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[157] *Mem. G.S.I.*, **40**, Pt. 3, 338.
[158] *Mem. G.S.I.*, **14**, 118-9.
[159] *Italics* by writer
[160] *Mem. G.S.I.*, **40**, Pt. 3, plates 74, 76, 81, 85.

due also to the fact that this deposit has resisted any dynamic metamorphism; and that rather than undergo any internal change these plastic semi-fluid beds have given and slipped and carried the overlying strata with them? Dr. Christie evidently recognised something of this character when criticising the question of intrusive origin of the red salt marls (see p. 484). As soon as the earth-movement reached a sufficiently high degree of intensity these mobile beds were squeezed into regions of relatively low compression thus readily forming the inverted fold. Further lateral pressure gave rise to fracture of the limb of the inverted fold and the over-fold was thrust forward, the clay serving as a lubricant along such thrust plane. We have remarked the frequency with which such beds are found in the thrust planes. The following examples will serve as illustrations of such occurrences. Fig. No. 4 shows these gypsum beds in the southern thrust between the Tarkhobi and Khulgai Nullas. About one mile west of the Panoba Gorge on the southern face of the limestone range two small outcrops of these marls are mapped. These mark the thrust plane on which the Murree synclinal so well shown in Fig. No. 5 was carried southwards. The Diagrams Nos. 2A and 2B in Middlemiss's work and from Wynne's paper on the Saline Series also show the red marls in thrust planes.

Had these remarkable deposits not been present, the strata would have withstood much more pressure before fracturing, and alterations of the structure and changes in the composition of the rocks would have taken place. Middlemiss recognised the varied development of dynamic metamorphism in new sedimentaries and crystalline rocks as seen by the following remarks :—[161]

"Lateral stresses if sufficiently powerful and long continued, acting on such a material (*i.e.*, crystalline rocks) would be unable to violently fold and plicate them on a large scale, but would spend themselves in minute deformation of the rocks, in shearing and in other ways characteristic of dynamic metamorphism."

In this region we have had the reverse case, which accounts for the absence of metamorphism in this region. Wynne realised that these marls had played a notable part in the determination of the stratigraphy as evidenced by his following remarks :—[162]

"It (the red marls) may be found in the most complex association with various groups and through faulting it is brought into juxta-position with some of the very newest rocks of the series, or it may be apparently inconsecutively overlaid by various bands—a result of progressive displacement in most cases caused by the

[161] *Mem. G.S.I.*, **26**, 280.
[162] *Mem. G.S.I.*, **14**, 72-3.

dissolving of the salt or washing out of the marl from below the superior groups—*it thus continually makes its appearance among the Stratigraphic which it has itself produced.*"[163]

Again he says:—[164]

"So far as I can judge the structure of the range (the Salt Range) leads to the inference that its existence is due to complicated lateral compression under *unequal conditions of resistance*, which in a late Tertiary period developed itself in local disturbance along one or more lines of fissure coinciding with the uniclinal escarpments."

Too much emphasis cannot be placed on the results that such a rock as the gypsiferous red marls would produce under such earth-movement as it has here doubtless been subjected to; especially when it is remembered that it is intercalated between relatively hard massive unyielding bands of limestone. We have seen in the foregoing that so varied are its modes of occurrence, that it has even been assumed to be of intrusive origin. If the role played by this deposit be appreciated, the difficulties, which have hitherto confronted geologists in this region, are overcome.

Age and Horizon of the Petroleum.

Oil Seepages.—The following list[165] has been prepared to show the known oil seepages in this field, and also the strata from which the oil issues:—

Locality.	*Rock from which oil issues.*	*Remarks.*
Sakdal ..	Alluvium	Close to a small oblique fault cutting Murrees and Upper Nummulitics
Chharat ..	1. ditto (?)	Rock not stated, probably Lr. Chharat
	2. ditto (?)	Map shows it at junction of Murrees and Upper Nummulitics
Jafar ..	Murree Beds	Doubtful occurrence
Chak Dalla ..	1. Lower Nummulitics	In alternations of shales and limestones
	2. Glumal Sandstone (Cretaceous)	Doubtful occurrence
Golra ..	Lower Nummulitics (?)	See Pascoe's remarks: p. 397, *Mem. G.S.I.*
Ratta Hottar	Junction of Lower Nummulitics and Upper	These occur in the vicinity of the "Nummulitic Boundary Fault" of Middlemiss. Structure similar to that at Panoba
Saidpur ..	1. Lower Nummulitics	
	2. Junction of Lower and Upper Nummulitics	

[163] *Italics* by writer.
[164] *Mem. G.S.I.*, **14**, 58-9.
[165] Compiled from *Mem. G.S.I.*, **40**, Pt. 3.

	Locality.	*Rock from which oil issues.*	*Remarks.*
	Khairi Murat	1. Junction Lr. Chharat and Murrees 2. Junction Lr. Nummulitic & Murrees 3. Murrees	Reversed faults recognised and mapped here.
	Khaur ..	Murree Beds	Attock Oil Co.'s property
	Panova ..	1. Lower Chharat 2. Alluvium	See pp. 449-463.
	Kotehri ..	Lower Chharat	Over-thrusts probable
	Malgin ..	1. ditto 2. Salt	ditto mapped
Kohat	Jatta ..	Lower Chharat	
	Darangi ..	Salt	
	Lachi ..	Lower Chharat	ditto ditto
	Lakoni ..	ditto	
	Nundrakki ..	ditto	
	Bahadur Khel	Salt	See Dr. M. Stuart, *Rec. G.S.I.*, 50
	Kundal ..	1. Sandstone 2. Conglomerate 3. Red and drab clays	(?) Basal Eocene (?) Kamlial (Siwalik) ditto ditto
	Jaba.. ..	1. Lower Chharat 2. ditto	See pp. 463-468.
	Salgi.. ..	Junction of red marls and Carboniferous	(?) Overthrust in Lower Chharat.
	Mardwal ..	Junction Siwalik and Lower Nummulitic	
	Sahdewali ..	ditto	
	Kabbakki ..	Siwalik Sandstone	Near junction of Lower Nummulitics and Siwaliks
	Khewra ..	1. Salt 2. Carbonaceous Shales	(?) Basal Eocene

In the above list of thirty-six occurrences only nine seepages occur from undoubted Lower Chharat beds; three from Lower Nummulitics; two from possible Basal Eocene; one possibly from Cretaceous Sandstone; three from Murree beds; three from Siwaliks; four from the salt; and seven along various junctions of rock groups.

It is therefore clear that it is impossible to argue as to the true petroliferous horizon from this data. At Panoba we have seen that the association of the oil with the Lower Chharat beds is a fortuitous one, and not significant of the true oil horizon; so that again reduces the number of definite associations of oil with the Chharat beds.

Classification of Seepages.—The frequency with which the Chharat beds occurs in thrust planes has been emphasised.[166] We have also noted that some of these thrust planes represent the

[166] See pp. 456-460, 466-467, 469, 471, 480, 484-486, 492, 493.

westward extensions of the "Boundary Faults" of Middlemiss in the Hazara District of the Himalayan System.[167]

An examination of Dr. Pascoe's map (*Mem.G.S.I.*, pt. plate 70) in the light of this new knowledge, leads one to the conclusion that the known oil shows can be classified into the following groups:—

1. Those along the "Nummulitic Boundary Fault" and its westward extension, *e.g*, Saidpur, Golra, Chak Dalla, etc., to Panoba.

2. Those along the "Main Boundary Fault" and its westward extension, *e.g.*, Khairi Murat, Nundrakki and Lakoni.

3. A number between the above faults especially in the Kohat Hills, *e.g.*, Malgin, Kotehri, etc.

4. Those along the Siwalik-Lower Nummulitic junction in the Salt Range and its trans-Indus extension, *e.g.*, Kundal, Jaba, Mardwal, etc.

5. Two only along the junction of the Red Marls and the Paleozoic-Mesozoic rocks, *e.g.*, Salgi and Khewra.

6. A few occurrences in the Soan Valley, *e.g.*, Khaur, Dhulian, etc.

It would be too lengthy a process to examine in detail every known occurrence in each of the above groups, but it may be instructive to consider one from each, and see whether we can arrive at any generalisation in the light of the knowledge of the structure and stratigraphy that the detailed mapping has supplied.

Group 1.—*Example;* Ratta Hottar, Golra and Saidpur Seepages.[168] Dr. Pascoe's map (plate 70) shows that these occur along the Nummulitic-Murree boundary. This is a continuation of Middlemiss's "Nummulitic Boundary Fault." The detailed maps on the scale of four inches equals one mile (*Mem. G.S.I.*, **40**, plates 71, 73) and the sections (plate 72) show clearly that here is a similar type of structure of reversed folds and faults to those proved at Panoba, which is along the same general tectonic line. We are therefore perfectly justified in view of the knowledge of the Panoba occurrence in attributing the association of oil with Lower Chharat beds, not to the latter being the true oil horizon, but to the fact that both the oil and the Lower Chharat clays are prone to occur in thrust planes. The thrusts at this locality will doubtless prove on closer examination to be not one simple fracture as shown by sections A, B and C (plate 72), but a very complex series similar to those proved at Panoba. Doubtless the remarkable thinning out of the Nummulite Shales shown by Dr. Pascoe in his sections A and C (plate 72) need not be resorted to, but the outcrops can be

[167] See pp. 487-489

[168] *Mem. G.S.I.*, **40**, Pt. 3, 373-80, 392-7.

explained by thrusting. The wide extent of the Lower Chharat beds here may be due to their development along lines of thrust as we have seen is often the case in other localities. The irregularities, which Dr. Pascoe explains by remarkable thinning out of certain beds is doubtless due to the development of such over-thrusts.

At Chak Dalla a little west of this region under consideration, the remarkable absence of the "Mottled Limestone" along the northern limbs of the folds is explicable by the same tectonic structure.[169]

Our experience at Panoba, leads us therefore to the conclusion that here also the association of oil with Chharat beds is a fortuitous one and is not indicative of a Lower Chharat age of the oil. At Chak Dalla oil occurs in the Lower Nummulitic limestone and also probably in the Cretaceous sandstone. There are no known occurrences of the Lower Chharat beds in the immediate vicinity. Surely this fact supports the view advanced by the writer, that the oil is of Lower Eocene (Basal Nummulitic) age.

Group 2.—The evidence available of the occurrences at Khairi Murat and Nundrakki is so scanty, that it is impossible to follow the above plan. It is clear, however, from the data on map (*Mem. G.S.I.*, **40**, plate 79), that the former area is in the vicinity of a great over-thrust and here again we must attribute the occurrence of the oil to its association with thrust planes, and not to any particular rock group. One seepage here is from the Murree-Lower Nummulitic junction and the other from the Murree-Lower Chharat junction.

At Nundrakki, the oil is associated with Lower Chharat beds, but here also there is faulting. The same is found in the Kurar Salt locality further west.

All these properties occur along a general tectonic line, which is the westward extension of Middlemiss's "Main Boundary Fault" in the Hazara District.

Group 3.—The Malgin area may be taken as the type of this group. Plates 83 and 85 of Dr. Pascoe's Memoir show clearly the fact that the occurrence of the oil with the Chharat beds is not really a significant one, but is due to the accompaniment of both with the thrust planes. The similarity of the structure to that found at Panoba is so striking that nothing further need be said.

Group 4.—The Kundal and Jaba areas are typical of this group of seepages. The reader is referred top p. 463-478 for the characteristics of these localities. The same general conclusion is arrived at by the examination of these shows, *viz.*, that the association

[169] *Mem. G.S.I.*, **40**, Pt. 3, plate 73.

of the oil with the Lower Chharat beds is due to the fact that these beds are commonly found along thrust planes.

Group 5.—No detailed maps are available of any occurrence in this group. The seepage at Salgi is perhaps the best example,[170] but the Khewra one is the better known.[171] If we concede that the red marl and salt are of Eocene age, and its junction with the Cambrian beds at the latter and the Carboniferous beds at the former, are due to over-thrusting, such as we have proved at Jaba and Kundal, again the occurrence of the oil is explicable by migration along a thrust plane. Dr. Pascoe writes on p. 483 of his memoir: "In the salt at Khewra for instance, in the scarp of the Salt Range, the oil contamination occurs in all probability in the lowermost limb of an over-thrust anticline with a very gentle northerly dip."

Group 6.—The Khaur occurrence is an example of this group. It is well known and recognised that the Murree beds are a local and not the indigenous oil horizon in this area. Pinfold's map of this locality[172] shows a fault plane with an east and west trend across the whole area; though the sections leave it uncertain whether the author regards this as a normal or a reversed fault. The presence of a fault as mapped by Pinfold is strongly confirmatory of the views put forward in this paper; and there seems little doubt that this is a reversed fault furnishing evidence of the over-thrusting elsewhere prevalent in this field.

Evidence of Basal Eocene Age of Petroleum.—We have seen that there is no primâ facie evidence for the assigning of the oil to any particular group of strata. We can, however, say that it always occurs where Nummulitic rocks are over-thrust either upon themselves or upon older or newer strata. In some areas, it is found where only Lower Nummulitic rocks occur, so that the assumption is, that the true oil horizon is low down in the Nummulitic group. At Kundal the oil occurs in a sandstone, the age of which cannot be determined with any certainty owing to its disturbed relations. Both Dr. Pascoe and the writer, however, are of the opinion that it should be assigned to the Basal Eocene (Basal Nummulitic) group.[173] A similar sandstone was found at Nammal[174] in the Eastern Salt Range, and at Mulla Khel[175] in the Maidan Range, apparently conformably underlying Lower Nummulitic limestone (Hill limestone) at both localities. At both places, however, the

[170] *Mem. G.S.I.*, **40**, Pt. 3, 434-5.
[171] *Mem. G.S.I.*, **40**, Pt. 3, 438.
[172] *Mem. G.S.I.*, **40**, Pt. 3, plate 78A.
[173] *Mem. G.S.I.*, **40**, Pt. 3, 426. See pp. 471-473.
[174] See pp. 443-444.
[175] See pp. 444-445.

sandstones are not petroliferous, but are associated with coals and fossil wood. At Jaba the oil is issuing from a faulted anticline in the Middle Nummulitic limestone (*i.e.*, the Basal beds of the Lower Chharat stage). Below the Hill limestone in the core of this anticline, there will be found presumably the sandstones equivalent to those exposed at Nammal and Mulla Khel.

At Panoba, the oil is seeping from the Nodular limestone of Lower Chharat age, but has undoubtedly migrated to this bed along a thrust plane. The only favourable storage for oil here is in the anticline formed by the Hill limestone north of Tarkhobi village. Presumably in the core of this anticline under the Hill limestone sandstones equivalent to those found at Nammal and Mulla Khel will be found with the drill.

The evidence, while not conclusive, all points to the Basal Eocene beds being the true oil horizon and every known occurrence in the Punjab and North-west Frontier can be explained on this assumption, coupled with migration along a thrust plane. We know that Basal Eocene times were favourable for the entombment of vegetable matter, as coal beds are found at this horizon. Here, as in every other known oil-field, the area was in close proximity to land and shows shore conditions in Basal Eocene times. Dr. Pascoe recognised this, too, as on p. 484 of his memoir he says:—

"There is no reason why oil should not be found in the lowermost layers of the Lower Nummulitic (Cardita beaumonti zone), but no undoubted occurrences at this horizon are known."

Again it is evident from his remarks on the age of the oil at Golra, that he had a suspicion of the Lower Nummulitic age of the oil there, as he says:—[176]

"It is doubtful whether any of the oil from the seepages or that found in the wells is derived from the Lower Nummulitic; in my opinion it is more likely indigenous to the Chharat stage."

Arguments Advanced in Favour of Lower Chharat Age of Petroleum.—Up to the present, it has generally been held that the oil of this field is of Upper Nummulitic age. Wynne first recognised the fact that the petroleum was associated with Upper Nummulitic beds.[177] Pinfold definitely assigned it to the Lower Chharat stage, recognising that the occurrences in the Murree beds was due to migration.[178] Pascoe agreed with Pinfold and gave the following reasons for assigning this age to the oil:—[179]

"As we have seen, the vast majority of our natural occurrences are found in recognisable Nummulitic beds, and in the Lower

[176] *Mem. G.S.I.*, **40**, Pt. 3, 397.
[177] *J. Proc. Asiatic Soc. Bengal* (*N.S.*), 1918, **14**.
[178] *Mem. G.S.I.*, **40**, Pt. 3, 483-4.
[179] *Mem. G.S.I.*, **17**, Pt. 2, 61.

Chharat stage of that series. Of the exceptions, the most important is that at Khaur, where the seepages and all the oil so far obtained occur in the Murree beds. We have the option of assuming either that the oil is indigenous to the Murrees, which must in that case have been deposited under different conditions from those under which the rest of the series was laid down, or that the oil has migrated upwards from the Nummulitic beds below. Although the migration theory generally has always presented difficulties to me, I must admit that in this case, it seems the more probable view. . . . We do not yet know the vertical distance up which migration must have taken place for the oil to have attained its present position, but since both the Murrees and Upper Nummulitics are in all probability of no great thickness, the chances are that this distance is short. Perhaps the Upper Chharat limestones are absent and the upward movement of the oil from the Lower Chharat and its access to the overlying Murrees thus facilitated . . . In all other exceptions, *i.e.*, in all cases, where the oil occurs in rocks about whose age there is some doubt, it cannot be shown that even if the rocks themselves are not Nummulitic, the oil has not originated from Nummulitic beds below or in the immediate neighbourhood. It is significant that when the oil horizon can be definitely recognised, it is with the exception of Khaur, always found to belong to the Lower Chharat stage. When the latter is missing, as most of it seems to be along the northern margin of the Salt Range, the oil is found along the plane of unconformity which represents this absent stage."

The list given at the commencement of this chapter refutes the statement that the majority of the natural seepages are from rocks of Lower Chharat age. The plane of unconformity referred to in the last sentence quoted has been proved at Jaba to be a thrust plane.[180] It does not represent the Lower Chharat stage or the "absent stage." Our work in the Jaba area has proved that the Lower Chharat and even the Upper Nummulitic limestones are well represented in this portion of the Salt Range.[181] No previous worker in this field has recognised the over-thrust nature of the strata and the frequency with which the Lower Chharat beds occur in the thrust planes. In spite of the fact that Middlemiss believed it possible to trace his "Boundary Faults" westwards into this area, the significance of this fact does not appear to have been realised. It is clear from the above quotation, that Dr. Pascoe had some difficulty in accounting for the upward migration of the oil into the Murree beds. If we

[180] See pp. 465, 466, 467.
[181] See p. 464.

recognise that thrusting has taken place, it removes the difficulties regarding this vertical migration of the oil at Khaur and other places.

Criticism of Lower Chharat Age Theory.—We see, therefore, that the principal arguments in favour of a Lower Chharat age for the oil disappear, and that the association of the oil and these beds is due entirely to the fact that both are frequently found in thrust planes, and not to the former being the indigenous horizon of the latter.

At Panoba the thrust plane is cutting across beds lower in the sequence than the gypsiferous beds of the Lower Chharat series, and yet petroleum is found along the thrust. At Saidpur, seepages occur where there are no Lower Chharat beds exposed, and the same is true at Chak Dalla. There are numerous exposures of the red clays of Lower Chharat age under conditions favourable for the occurrence of petroleum, but they are not petroliferous, except when they occur in a thrust plane. The conclusion must be that the association of oil with the Lower Chharat beds is not that of oil with the particular strata, but of oil with a thrust plane. In every case where we know of oil there is nothing against its having been derived from Basal Eocene (Basal Nummulitic) beds, and where detailed examinations have been made this zone occurs under conditions such that it would provide a suitable site for the accummulation and storage of oil reserves. While agreeing with Dr. Pascoe that the petroleum is of Nummulitic age, the writer is strongly of the opinion that the balance of evidence is in favour of its Basal Eocene age.

Origin of Oil.—Dr. Pascoe has gone to considerable trouble to prove the association of the Punjab oil with coals,[182] and is evidently of the opinion that the origin of the two is related. This later work has suggested a yet more close association of the oil and coal of the Punjab. The writer is therefore in accord with Dr. Pascoe in attributing a vegetable origin to the petroleum of this field. Pinfold[183] undoubtedly supports the view expressed by Griesbach,[184] who was struck by the large foraminiferal (Nummulitic) life in the rocks and attributed the origin of the oil to the abundance of these organisms.

Summary and Conclusion.

The area in which this work has been done is one of considerable political unrest, so that field work was conducted with great

[182] *Mem. G.S.I.*, **40**, Pt. 3, 485-7.
[183] *J. Proc. Asiatic Soc. Bengal* (*N.S.*), **14**. *Rec. G.S.I.*, **49**.
[184] *Rec. G.S.I.*, **25**, Pt. 2, 107-8.

difficulty. Almost everywhere it was necessary to travel with a police guard, and to take elaborate precautions to prevent being sniped by independent tribesmen and out-laws while at work. Owing to this, and transport difficulties, no systematic collection of specimens was made, and it was impossible to follow up questions which entailed visits far from one's organised camp.

Many of the rocks of the area are fossiliferous and a paleontological examination would undoubtedly bring valuable knowledge to light. The question as to whether the unconformity, which doubtless occurs in many places between the Murree and the Nummulitic Series, is a wide-spread one, needs further examination. With this is involved the definite classification of the purple and red clays and sandstones, which are sometimes mapped with the Murrees and sometimes with the Lower Siwalik (Kamlial).

It is hoped, however, that the present work will have gone some distance towards the solution of some of the many difficulties presented in this region.

The following facts may now be regarded as established:—

1. There was an outbreak of igneous activity as in Sind, in Cretaceous times, which outbreak was probably associated with that yielding the Deccan traps.

2. In early Eocene times, portions of this area was a land surface, as proved by the lateritisation of the above-mentioned igneous rock.

3. The plication, over-folding, and over-thrusting of the strata took place here in post-Siwalik times, and was due to lateral movement and not to vertical uplift.

4. The structures here developed have many points in common with those found in the Himalayan System and these hills should be included in the Sub-Himalayan zone of that system.

5. The "Boundary Faults" of the Himalayan System of the Hazara District can be traced westwards into this area as "Thrusts."

6. The red marls of the Salt Range owe their varied characteristics and associations to the fact that they have been over-thrust upon and among other strata.

7. These marls are largely responsible for the "Stratigraphical wreck" produced.

8. They are not of intrusive origin, but owe their likeness to such rocks to their having been squeezed along thrust planes and into flexures.

9. They are not of pre-Cambrian age, but are the equivalents of the similar red marls of Lower Chharat age (Eocene) of the Kohat Hills. Presumably the salt of both areas is on the same age (Eocene).

10. The true oil horizon is not the Lower Chharat beds but the

Basal Nummulitic, and the association of the marls and the oil is due to both being associated with thrust planes.

The writer is greatly indebted to previous works on the geology of this area, particularly to those of Mr. A. B. Wynne, Mr. C. L. Griesbach, Mr. C. S. Middlemiss and last but not least to those of Dr. E. H. Pascoe.

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Contribution to the Knowledge of Polymerisation. Part I.

By H. I. Waterman, Ph.D., and J. N. J. Perquin. (With the collaboration of G. F. de Ridder and J. P. Kuipers.)

Gurwitsch[1] gives some important facts relating to the polymerising of hydrocarbons. Some unsaturated hydrocarbons will polymerise at ordinary temperatures and without the addition of an agent, *e.g.*, cyclopentadiene will change to dicyclopentadiene. Many other examples are given, such as styrol, etc. The well-known experiments of *Engler*, who from an increase in specific weight and boiling point after the heating of hexylene to 360-365° C. (in sealed tubes) concluded to polymerisation. This process was also associated with a decrease of the bromine number. There is no doubt that we have in the first place a destruction of the hexylene by high temperature.

Gurwitsch next outlines the acceleration of polymerisation by the influence of catalysers, such as H_2SO_4, $AlCl_3$. In some cases porous substances, such as bleaching earth, activated carbon, etc., would cause polymerisation of unsaturated hydrocarbons (amylene, pinene) without external heating, and in some instances considerable heat would be liberated and frequently would cause boiling of the mass.

It is remarkable that in general very few details are given in connection with the purity of the hydrocarbons. Little attention is given to the ultimate analyses of the products before and after the process. This is of importance, because we definitely know that traces of oxygen can cause decomposition of hydrocarbons at a relatively low temperature.

In practice also the polymerisation problem is of importance. We agree with *Gurwitsch* that crude oil, as found in nature, will not polymerise further when kept at normal temperature, as such polymerisation would have taken place previously.. With distillates, however, and particularly with cracked products, the phenomena of polymerisation may show. With cracked spirit, polymerisation may occur when the spirit is kept at ordinary temperatures, or during refining.

The authors have carried out a systematical research on the action of porous substances on unsaturated hydrocarbons, the

[1] L. Gurwitsch, Wissenschaftliche Grundlagen der Erdölverarbeitung, Berlin, 1924, 2e Aufl.

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Hydrocarbon, formula, bromine number and refraction (n_D).	Origin.	Without porous substance.		With porous substance.			
		Distillation.	Distillate.	Porous substance used.	Duration of contact.	Distillation.	Distillate.
AMYLENE (C_5H_{10})— Bromine number, determined, 220; theoretical, 229. n_D, 21·3°, 1·3801.	Poulenc frores, Paris.	Almost entirely between 25° and 45°.		Industrial silica gel, activated in lab. at 200°, 23 per cent. by weight.	1 hr.	Between 25° & 45° the percentage of distillate was nearly equal to that without the porous substance.	Bromine number, 218. n_D, 21·3°, 1·3800.
HEXYLENE (C_6H_{12})— CH_3—CH=CH—C_3H_7. Methylpropylethylene. Bromine number, determined, 178, 180; theoretical, 190·5.	C. A. F., Kahlbaum. Berlin.	At about 60° to 75°, >90 per cent.	n_D, 20·3°, 1·3950.	Silica gel, 47 per cent. by weight.	1 hr.	65° to 70° and 80°. Colourless distillate >90 per cent.	Bromine number, 176, 181. n_D, 20·3°, 1·3950.
CAPRYLENE (OCTYLENE)— (C_8H_{16})— Bromine number, determined, 112, 112, 112; theoretical, 143. n_D, 20·2°, 1·4212.	Th. Schuckardt, Gorlitz	First drop at 90°, temperature rise regular to 124°, constant 124° to 126°, 87 per cent. at 207°.	Bromine number. 117, 119. n_D, 20·5°. 1·4169.	Floridin XXF, H. Bensmann, Bremen. 53 per cent. by weight.	24 hrs.	First drop at 92°, temperature rise regular, no constant b.p., 79 per cent. at about 150°.	Bromine number, 119, 119. n_D, 20·6°, 1·4165.
HEXADECYLENE ($C_{16}H_{32}$)— $CH_3(CH_2)_{13}$—CH=CH_2. Bromine number, determined, 62, 63; theoretical, 71. n_D, 21·3°, 1·4406 n_D, 19·5°, 1·4417.	C. A. F., Kahlbaum, Berlin.	B.p. 270° to 275°, almost complete distillation at this temperature, only small quantity left in flask.	Colourless. Bromine number 64. n_D, 19·6°, 1·4415. n_D of residue, 20·5°. 1·4457.	New Filtrol, heated for about 6 hours at about 200° and cooled in exsiccator. 28 per cent. by weight.	48 hrs.	First drop at about 96°, temperature rises regularly to 335°, over 80 per cent. distilled.	Bromine number, 45, 47. n_D 19·6°, 1·4430.
DIALLYL— CH_2=CH—CH_2—CH CH_2 Divinylmethane. Bromine number, determined, 356, theoretical, 471.		50° to 61°, 95 per cent.	Bromine number, 314, 322, 331, 332, 334, 342, 353. n_r, 19·9°, 1·4079.	Silica gel, 79 per cent. by weight.	1 hr.	50° to 62°, 90 per cent.	Bromine number, 316, 328, 341, 342, 344. n_D, 10 3°, 1·4074.
"ESSENCE CATALYTIQUE"— Yellow liquid. Bromine number, 64. n_D, 21°, 1·4632.	Trade product.	60° to 190°, 95 to 96 per cent. of pale yellow distillate.		Bauxite, heated for 1½ hrs. at at 500°, and cooled in exsiccator. 42 per cent. by weight.	35 min.	I.b.p. 40° to 50°, 95 per cent. of distillate (yellow) to 202°.	Bromine number, 63, 64, n_D, 21°, 1·4637.
Ditto				Floridin, 46·5 per cent. by weight.	2 hrs.	64° to 190° about 94 per cent.	Bromine number, 61, 61. n_D 21°, 1·4630.
D. PINENE— Bromine number, 169, 170.	C. A. F., Kahlbaum, Berlin.	151° to 160°, almost 100 per cent.	n, 19·8°, 1·4669.	Franconite, heated for ¾ hr. at about 400°, 63 per cent. by weight.	1½ hrs.	158° to 250°, 63 per cent.	The distillate, after drying with sodium sulphate, was completely clear. Bromine number, 40,39, 41. n_D, 19·9°, 1·4756. The residue was a black gummy mass.
Ditto				Franconite, used without previous heating.	2 hrs.	First drop at at 100°, main percentage at 150° to 160°, maximum temperature 210°, 76 per cent.	The distillate, after drying with sodium sulphate, was completely clear. Bromine number, 130, 133, 126, 124, 121, 126, 123, 121. n_D, 20·3°, 1·4711. Drips at end of distillation: Bromine number, 38. n_D, 20·4°, 1·4765.
L. PINENE— Bromine number, 99, 100. n_D, 19·8°, 1·4700.	C. A. F., Kahlbaum, Berlin.			Carboraffin dried at 130° in stream of dry air.	48 hrs.	First drop at 150°, end-point at 163°, 73 per cent.	Bromine number, 114, 95, 89, 104, 96, 97.
Ditto				Exposed for 44 hrs. to dark electric discharges in de Hemptinne apparatus (absolute hydrogen pressure), 10 cm. mercury.			Bromine number, 96, 96. n_D, 20°, 1·4710.
PINENE ($C_{10}H_{16}$)—							

Bromine number, 169, 170.	C. A. F., Kahlbaum, Berlin.	151° to 160°, almost 100 per cent.	n, 19·8°, 1·4669.	Franconite, heated for ¾ hr. at about 400°, 63 per cent. by weight.	1½ hrs.	158° to 250°, 63 per cent.	The distillate, after drying with sodium sulphate, was completely clear. Bromine number, 40,39, 41. n_D, 19·9°, 1·4756. The residue was a black gummy mass.
Ditto				Franconite, used without previous heating.	2 hrs.	First drop at at 100°, main percentage at 150° to 160°, maximum temperature 210°, 76 per cent.	The distillate, after drying with sodium sulphate, was completely clear. Bromine number, 130, 133, 126, 124, 121, 126, 123, 121. n_D, 20·3°, 1·4711. Drips at end of distillation: Bromine number, 38. n_D, 20·4°, 1·4765.
L. Pinene— Bromine number, 99, 100. n_D, 19·8°, 1·4700.	C. A. F., Kahlbaum, Berlin.			Carboraffin dried at 130° in stream of dry air. Exposed for 44 hrs. to dark electric discharges in de Hemptinne apparatus (absolute hydrogen pressure), 10 cm. mercury.	48 hrs.	First drop at 150°, end point at 163°, 73 per cent.	Bromine number, 114, 95, 89, 104, 96, 97. Bromine number, 96, 96. n_D, 20°, 1·4710.
Ditto							
Pinene ($C_{10}H_{16}$)— Colour, pale yellow. Bromine number, determined, 171, 175, 177. n_D, 25°, 1·4641.	Prepared from turpentine oil.	Over 90 per cent. at 135° to 155°.		Industrial silica gel activated at 200°, 48·5 per cent. by weight.	1½ hrs.	Over 90 per cent. at 100° to 155°.	Bromine number, 173, 177. n_D, 25°, 1·4647
D. Limonene— Bromine number, determined, 205, 206; theoretical, 235. n_D, 19·8°, 1·4740.	Th. Schuckardt, Gorlitz.	First drop at 167°, temperature gradually increases to 175°, constant for long period at 176° to 177°, then rapid rise to 182° 95 per cent. at 250°.	Bromine number, 201, 207, 215, 208·5, 216, 217. Duration of bromine action, 1 min., 2 min., 2 min., 7 min., 7 min. n_D, 19·7°, 1·4742.	Supra - Norit, 42·3 per cent. by weight.	5 hrs.	First drop at 95°, temperature gradually increasing Nearly 95 per cent. at 250°.	Bromine number, 211, 214. Duration of bromine action, 2 min. n_C, 19·6°, 1·4737.
L. Limonene— Bromine number, deter-	Th.	First drop at	Bromine num-	Supra - Norit,	4½ hrs.	First drop at	Bromine num-

		period at 176° to 177°, then rapid rise to 182° 95 per cent. at 250°.	min., 2 min., 2 min., 2 min., 7 min. n_D, 19·7°, 1·4742.			cent. at 250°.	1·4737.
L. LIMONENE— Bromine number, determined, 199, 201. Duration of bromine action, 18 min. n_D, 19·8°, 1·4753.	Th. Schuckardt, Gorlitz.	First drop at 165°, temperature increases to 168° to 170° and remains constant for a short time. End point, 235°, 93 per cent.	Bromine number, 205, 206. Duration of bromine action, 11 min. n_{α}, 20°, 1·4747	Supra - Norit, 44 per cent. by weight.	4¼ hrs.	First drop at 104°, b.p. constant at 165° to 168°. Over 96 per cent. at 235°.	Bromine number, 182, 180. Duration of bromine action, 17 and 11 min. n_D, 19·9°, 1·4752.
STYROL— $C_6H_5CH=CH_2$. Bromine number, determined 135, 135, 136; theoretical, 154. n_{Li}, 21·2°, 1·5429.	Th. Schuckardt, Gorlitz.	First drop at 100°, temperature rise regular to 144°, 90 per cent.	Completely clear. Bromine number, 133, 134. n_D, 20·3°, 1·5428. Residue easily gives cobweb-like threads. Bromine number, 47. n_{Li}, 19·8°, 1·578 (observation difficult).	"Silica," previously heated. Loss on heating, 7·8 per cent. by weight. With xylene distillation method a water content of 5 per cent. was found before the heating. 40 per cent. by weight.	3 hrs.	First drop at 150°, temperature increasing to 205°. Only 15 per cent.	Colour, yellow. Bromine number, 1·5. n_D, 21°, 1·5117.
STILBEEN— $C_6H_5—CH=CH—C_6H_5$. Bromine number does not give constant results; theoretical, 88·9. Melting-point, 113° to 124°.	C. A. F., Kahlbaum, Berlin.			Activated silica gel. 50 per cent. by weight.	Heated for 1 hr. in oil bath at 150°	300° to 320°,	Colourless. Bromine number does not give constant results. Melting-point, 113° to 121°.
INDENE (C_9H_8)— Bromine number, 134, 135. n_D, 20·3°, 1·5760. Ditto	Th. Schuckardt, Gorlitz.	First drop at 170°, temperature constant for long period at 179° more than 95 per cent. at 188°.	Colourless Bromine number, 135, 136, n_D, 21·3°, 1·5743.	Floridin, XXF, H. Bensmann, Bremen. 29 per cent. by weight.	24 hrs.	First drop at 125°, temperature increasing gradually to 286°, 88 per cent.	n_D, 20·7°, 1·5820.
				Fuller's earth, XXF, Floridin Co., Warren, Pa. (H. Sommer, Bremen). 57 per cent. by weight.	24 hrs.	First drop at 144°, temperature constant for short time at at 163°. End point, 205°, 49 per cent.	Bromine number, 116, 117. n_D, 21°, 1·571. (accurate determination could not be made).

DETERMINATIONS OF MOISTURE (exclusive of those given in Table).

	Fuller's earth, H. Sommer, Bremen.	Floridin.		Franconite.	Silica gel. (a)	New Filtrol.	Supra-Norit. (b)
			H. Bensmann.				
Loss of weight during heating for some hours, per cent.	18·1	20·9	18·6	23·4	10·3	22·7	23·4
Xylene method, per cent.	11·0	—	11·0	—	7·0	17·0	22·8

(a) The activated product was kept in an exsiccator with $CaCl_2$, and at each opening some moisture may have been taken up.
(b) Was heated only to 250° for some hours.

hydrocarbons being kept in contact with a definite quantity of bleaching earth, or active carbon, for a determined length of time. The product was measured and distilled, its properties (Bromine Number, McIlhiney method, and Refraction) being determined. and the results compared with those obtained by distillation under comparable conditions, but without porous substance. The results are given in the table.

The liberation of heat observed sometimes on the mixing of the unsaturated hydrocarbons with the porous substance is not always accompanied by a transformation of the hydrocarbon.

Hexylene and silica gel became warm on mixing, in the same way as diallyl and silica gel, d. pinene and franconite (previously heated to about 400°), so that a phenomena is observed which resembles boiling of the liquid. Franconite, not previously heated, gave no liberation of heat. l. Pinene became warm with carboraffin (previously dried) and styrol, on mixing with "Silica" (previously heated and cooled), became very warm, the mass becoming brown-black and finally solid. With Supra-Norit, d. limonene became warm, while l. limonene did not liberate any heat. Hexadecylene and filtrol (previously heated to 200° and cooled) caused very little evolution of heat, and caprylene and indene respectively with Floridin XXF (Bensmann) gave practically no heat. In those experiments where much heat was liberated, the product was changed. The humidity of the porous substance proved to be of importance, as in the case of experiments carried out by C. Jamin, and the necessity for drying the floridin to activate it has also been pointed out by *S. W. Lebedew* and *E. P. Filonenko* in their research work on polymerisation.[2] This is also proved by the two samples of franconite, one previously heated and the other used without being heated.

In our experiments distillation temperature was important. The velocity of the reaction is accelerated by high temperature and there is also an indirect influence in experiments where temperatures in excess of 100° are reached, where there is a loss of water in the porous substance in the flask, causing an acceleration of the reaction, *e.g.*, with indene and floridin at 140-150° there is a considerable increase in the reaction.

From these experiments it is seen that substances active in respect of decolourising and desulphurising power, such as silica gel, need not necessarily change a product like amylene. The silica gel used was certainly active in its decolourising and desulphurising action, although this action was not ultimate. The amylene treated was very slightly, if at all, changed, as also was

[2] *Ber.*, 1925, **58**, 163.

hexylene, diallyl and pinene. The same holds also for Supre-Norit in its action on d. and l. limonene, and for floridin treated with "essence catalytique." It is possible that in these examples a fugitive change (polymerisation) occurred, the original product being recovered on distillation.

In addition to the boiling point, the boiling range and the quantity of distillate, we also compared the refraction and the Bromine Number (addition, McIlhiney method). The constants determined, particularly the Bromine Number, have not an absolute value as the hydrocarbons used were not quite pure. This also explains the increase of the Bromine Number caused by distillation. The Bromine Number of the distilled octylene (117 and 119) was higher than for the original product (112) and the distilled hexadecylene gave 64 against 62 and 63 before distillation. Some products, like diallyl and stilbene, gave very irregular results for the Bromine Number, and pinene also gave bad results. The duration of the action of bromine in CCl_4 solution when determining the Bromine Number, except in the cases mentioned in the table, was always 1 to 2 minutes, and the length of time was proved to influence the results with limonene. The impression was given that bromine addition will not be of value in the analysis of hydrocarbon mixtures, but further research proved otherwise. A series of aromatic hydrocarbons gave the following numbers:—

	Addition (percentage of weight of bromine).		
		After purification.	After further purification.
Benzene	0·1, 0·7, 0·8 0·7, 0·5 ..	0·1 ..	—
Toluene	0·8, 0·6 ..	0·5, 0·8 ..	0·6, 0·7
Xylene (*a*)	2·7, 2·7, 2·6 2·5 ..	— ..	—
Mesitylene	1·8, 1·6 ..	0·5 ..	0·3, 0·2
Naphthalene	3·6, 3·0 ..	— ..	—
Phenanthrene (puriss. Kahlbaum)	8·3—12·5 ..	— ..	—

(*a*) Mixture of different isomers.

Benzene has a low Bromine Number, and the alkyl derivatives also give low values, although the latter are generally higher than those of benzene. Purification with concentrated sulphuric acid causes a lowering of the addition number, but the addition of zero with the alkyl derivatives was not reached. The higher aromatics, naphthalene, phenanthrene, had Bromine Numbers somewhat higher than for benzene.

When these figures are compared with the behaviour of the olefines, amylene, hexylene, octylene and hexadecylene, it is found that the olefines do not give the theoretical values, but the Bromine Numbers are not much lower relatively than the calculated values.

The discussion of these results in a quantitative sense serves no use as the hydrocarbons are not as pure as can be desired. It is even known that the purity of the liquid saturated hydrocarbons of the methane series is not certain. The constants given in literature differ considerably, and it is absolutely necessary that the more important hydrocarbons should be prepared in a pure condition.

Various hydro-aromatic hydrocarbons gave the following results:—

	Bromine number (addition).
Cyclohexane (Kahlbaum)	0·4, 0·6
Methycyclohexane (Poulenc)	2·3, 2·2
„ (Schuckardt)	0·2, 0·5
Metadimethylcyclohexane (Poulenc)	1·3, 1·7
„ (Schuckardt) ..	0·6, 0·9

A series of samples of saturated hydrocarbons gave:—

	Bromine number (addition).
n-Pentane (Poulenc)	1·6, 1·6
„ (Schuckardt)	3·0, 3·2
Isopentane (Poulenc)	1·4, 1·6
n-Heptane (Poulenc)	2·1, 2·0
„ (Schuckardt)	1·3, 1·0
n-Octane (Schuckardt)	5·0, 4·6

(Aethylidenebromine $CH_3CH\ Br_2$, b.p. 108°—108·2°, a sample received from Prof. Wibaut, Amsterdam, gave a bromine number (addition) of 0·1, two observations.)

These saturated bodies gave low Bromine Numbers, which could be expected, but how far a contamination causes the stated addition numbers, or how far this is caused by the hydrocarbons as such, could not be ascertained with the samples used. Various hydrocarbons, such as diallyl, pinene, etc., gave deviating results, but we consider that the results obtained are sufficient to conclude with certainty that the determination of the Bromine Numbers by the McIlhiney method is of use in the analysis of many hydrocarbon mixtures.[3]

[3] See also H. I. Waterman and A. F. H. Blaauw, "Further Investigation in the Liquid Reaction Products obtained by the Action of Hydrogen on Paraffin Wax under High Pressure at 450°," *Rec. trav. chim.*, 1926, **45**, 284.

Contribution to the Knowledge of Polymerisation. Part II.

By H. I. Waterman, PL.D., and J. C. Jamin.

It is usually supposed that polymerisation occurs when a liquid hydrocarbon or an oil is thickened or if the boiling point of the hydrocarbon is raised. In many cases the molecular weight and the halogen number are seldom determined, and only very rarely is there any control if the elementary composition remains constant. *Amylene* (Kahlbaum, Berlin) was the unsaturated hydrocarbon experimented upon in this research. The amylene was weighed into a distillation flask and *norit* (carbon), was added in the proportion of about 2 parts of amylene to 1 of norit. On mixing, a rise in temperature was always observed. The mass was left in the flask, for 28 hours[1], after which a distillation was carried out at room temperature and at an absolute pressure of 2·5 c.m. mercury, until nothing more could be distilled off. The vapours were condensed by cooling with solid CO_2 and alcohol.

A quantity of hydrocarbon remained in the norit after distillation, the amount depending on the moisture-content of the norit. In connection with the moisture-content of this species of carbon, it was found that when the norit was dried before use (heated to 130° C and dried over P_2O_5) a greater quantity of hydrocarbon remained in the carbon after distillation. The determination of moisture-content of the norit was effected by distillation with xylene, and thus it was found that the "air-dry" norit contained 22·7 per cent. of water, while the sample, dried at 130° (to a constant weight) gave 21·5 per cent.

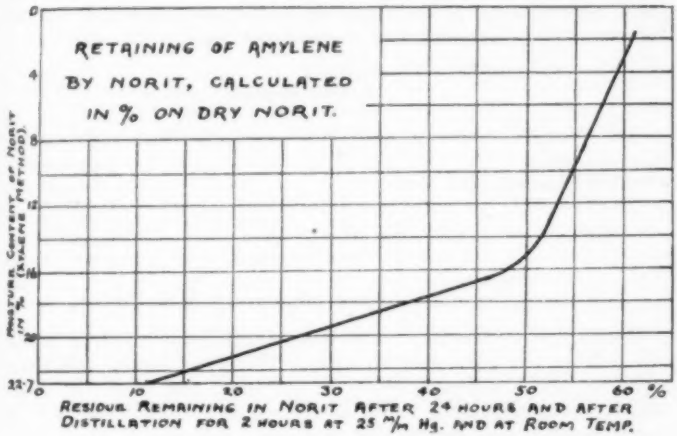
The refraction of the distillate differed but little from the original substance :—

n_D of the original amylene	1·3863 (18·8°)
n_D of the distillate obtained by treatment with air-dry norit (in the flask there remained 9·6% calculated on dry norit)	1·3853 (18·9°)
n_D of the distillate obtained by treatment with norit dried at 130° and afterwards dried with P_2O_5 at ordinary temperature (in the flask there remained 63·1 % calculated on dry norit)	1·3849 (18·9°)

After these preliminary experiments a competitive research was carried out, the result being plotted in the accompanying

[1] In the experiments which were carried out later the time of contact was 24 hours.

graph. From the curve, it will be seen that a relation exists between the moisture-content of the norit and the quantity of hydrocarbons which remains after distillation, calculated on dry norit. It can clearly be seen that the smaller moisture-content of the norit, the higher is the percentage of material retained by the carbon. Between the limits of 22·7 and 16 per cent. the influence of moisture is most marked. The substance remaining in the norit could not be expelled by heating to 40° C. in a vacuum. The same negative result was obtained when trying to dissolve the remaining hydrocarbon in camphor; at least, the melting point did not change (norit also does not change the melting point). However, the formation of a film was observed in the upper part



of the tube in which the camphor, with the norit residue, was heated to just above the melting point of camphor (± 177°). In addition, the adhering hydrocarbon did not dissolve in heptachlorpropane, stearic acid or diphenylamine, and in each case the melting point of these substances did not change.

Influence of *pumice-stone*. In one experiment where the boiling point of the amylene was determined, some pieces of pumice-stone were added, in order to secure regular boiling. The initial boiling point of the amylene was 35° but the temperature was raised to more than 50°, while the distillate had a smell somewhat resembling turpentine. Still more noticeable was the turpentine smell of the residue which remained in the distillation flask together with the pumice-stone. Now the distillate was distilled once

more without pumice-stone, up to 39°. The distillate which was then obtained had very little smell of turpentine ((n_D of this distillate : 1·3855 (19·5° C.))). The residue in the flask was present partly in the pumice stone and partly in the form of liquid ((n_D : 1·4320 (19·2° C.))). Therefore, the pumice-stone has an influence on the amylene and changes this substance under the circumstances just mentioned. That the pumice-stone itself, and not the distillation as such had caused the alteration of the amylene was proved by an ordinary distillation of the original amylene the regular boiling now being promoted by the addition of some pieces of glass. The boiling point of the greater part was 35-36°.[2] The *bromine number* (addition method of Mc. Ilhiney) and the *refraction* of the *distillates* obtained in different experiments with norit, proved that (apart from the substance remaining in the "carbon") the amylene had *changed but little.*

	Moisture-content of the norit. %	Bromine addition.	Number substitution.	n_D
Original amylene		210	9	1·3838 (25°)
Distillate obtained after treatment with norit	1·6	213·6	10·8	1·3828 (24·7°)
" " " ..	13·0	210·8	11·4	1·3826 (24·2°)
" " " ..	16·0	211·4	11·4	1·3830 (23·4°)
" " " ..	18·6	211·2	11·2	1·3832 (22·7°)

Examination of the Amylene-Residue left in the Carbon.

It was now necessary to determine whether the amylene which was left in the norit had changed. Therefore, larger quantities were employed, namely, 20·27 Gr. amylene, and 15·07 Gr. norit, which, by drying for 4 hours at 125° C. had been brought to a moisture-content of about ±1·6 per cent. (xylene method). After 24 hours this mixture was distilled over a period of 2 hours at room temperature in a vacuum (pressure 25 m.m. mercury). There remained in the norit 6·18 Gr. this quantity being less than in the first series of experiments ; the proportion of weight between norit and amylene, however, was different. The apparatus used, consisted of a vacuum oil-pump and a vessel containing cocoanut coal, cooled with liquid air for obtaining a still higher vacuum. Connection with a Geissler tube indicated that a high vacuum could be attained in this apparatus. The successive parts of the apparatus were :—(1) Distillation flask containing the norit with amylene-residue, (2) the condenser directly connected with the distillation flask and placed in liquid air, (3) the Geissler-tube.

[2] It is probable that a mixture is being dealt with.

(4) The vessel containing cocoanut carbon. (5) The main connected with the oil-pump. At ordinary temperature no distillation took place, but when the temperature had reached about 160° C. (determined in the air-bath close to the distillation flask), a distillate was obtained. After one hour two layers of liquid could be observed in the condenser (distillate 3·2 Gr.). Distillate I was taken out of the condenser, and after increasing the temperature to 240° C., the second distillate (II) was taken from the condenser (1·0 Gr.). The total quantity of distillate was 4·2 Gr., while the loss was 0·75 Gr. Of the missing 6·18–4·95=1·23 Gr., only 0·4 Gr. had been left in the norit. The loss therefore was about 0·8 Gr. The upper layer of distillate I had a bromine number (addition) 208·5 substitution 8·9 refraction n_D 1·3914 (18·7° C.). A distillation carried out on 2 gms. of this product showed the initial boiling point to be 35° C., while 1·7 gms. distilled off up to 40° C. (n_D 19° C.: 1·3896). The residue from the distillation had a refraction n_D 19° C.: 1·4240. From a consideration of the constants of the original amylene, it can be concluded that the amylene from distillate I has been contaminated with higher boiling products. As will be indicated later, the original amylene contained only a limited quantity of higher boiling product.

It can be expected that these higher boiling products will be absorbed by the norit more readily than the pure amylene, the result being that an accumulation of impurities will be found in the amylene-residue which remained in the carbon. From this point of view, it is probable that the observed higher refraction is not caused by polymerisation and if the latter had occurred, it would only have been in very small quantities. The lower layer of distillate I was completely miscible with water and was chiefly identified as such. During the distillation of distillate II there was a loss of 0·75 Gr., the remaining 1·0 Gr. had a refraction n_D 19° C.: 1·3934, bromine number (addition) 202·2, substitution 10·0. From these figures and also from the above considerations, it can be concluded that distillate II also contains chiefly amylene.

Lebedew and Filonenko[3] having studied the activity of floridin towards *iso*butylene-vapour it was decided to investigate, in addition, the behaviour of amylene-vapour towards dried floridin and dried norit.

Experiment with Dried Floridin.—The floridin used (Bensmann XXF), was heated for 2 hours with stirring at 290-300° C., and was then cooled in a dessicator with P_2O_5. The apparatus used by Lebedew and Filonenko was used in this investigation, 6·20 Gr. of floridin was placed on the glass-wool, and in order to prevent any condensation of

[3] *Ber. der Deutschen Chem. Ges.* **58**, 163 (1925).

amylene in the floridin, a circulation of water was provided (temperature 45°-50° C.) in the cooling mantle. The tube holding the floridin was connected to a flask containing 50 Gr. of amylene. By means of CO_2 dried with H_2SO_4 at the beginning of the experiment, the air was driven out of the apparatus, after which the amylene in the flask was heated and the vapours of the boiling substance conveyed to the floridin, which was kept at the stated temperature. Of the quantity of amylene used, 4·6 Gr. was not evaporated, and 2·3 Gr. of the vapours remained in the floridin. 15·2 Gr. of liquid product was obtained in the receiver, which was placed under the floridin tube, while in a vessel cooled with liquid air and connected with the receiver, 24·6 Gr. of a liquid product was condensed. There was a total loss of 3 Gr. The amylene residue in the floridin was driven out by heating under high vacuum for 2 hours at 170°. 2 Gr. of condensate was separated, and the following constants determined :—The bromine number, refraction and spec. weight of the original amylene (A) the residue of the evaporation (B) the liquid driven out by the heating of the floridin in high vacuum (C) the distillate (D) obtained in the receiver under the tube filled with floridin and finally of the condensate (E) obtained in the vessel cooled with liquid air. In addition, for the purposes of comparison, the properties of another evaporation-residue (F) of the amylene, used in an earlier experiment were determined.

The results obtained are tabulated below :—

	Bromine number addition	Bromine number substitution.	n_D.	Sp. gr. $\frac{19°}{4°}$ C.
A	215·2	9·8	1·3832 (23·1° C.)	0·670
B	114·2	8·8	1·4212 (22·5° C.)	0·758
C (2·0 Gr.)	78·1	47·9	1·4330 (25·0° C.)	0·773
D	218·2	9·8	1·3840 (22·8° C.)	0·667
E	222·1	10·0	1·3820 (23·1° C.)	0·666
F	89·4	6·3	1·4338 (24·2° C.)	—

From the above results it can be concluded that the product had undergone an alteration. The amylene was evaporated from the flask until a temperature approaching 45° C. had been reached and notwithstanding this, there remained 2·3 Gr. in the floridin. In addition, the amylene-residue had a very high refraction and spec. grav., while the bromine number had been decreased considerably. These alterations of constants could not be ascribed to the operations which the product had undergone, as will be proved by the analogous experiment with norit (see below). It was observed that the amylene-residue in the floridin had similar properties to the two evaporation-residues B and F, with the exception of the behaviour towards bromine in connection with

the substitution. The cause of the last mentioned difference cannot be explained at present. It is interesting to note that the bromine number of the most volatile amylene fraction (E) is the highest, and approaches the theoretical value, the bromine number of D is also higher than that of A. It might be possible that the change in properties of the evaporation-residues B and F, when compared with the amylene, is due to a similar reaction as that brought about by the floridin. It is impossible to state definitely, whether in this case the change is due to polymerisation, until the elementary analysis has proved this with certainty.

The experiment was repeated, but instead of floridin, norit (dried to ±1·6 per cent. of moisture) was used, the quantities being 40 Gr. amylene (A) and 4·32 Gr. norit. The residue of evaporation of amylene in the flask, in this case was 4·0 Gr. (B); the amylene-residue in the norit was 2·06 Gr. (C), the condensate (D) under the tube with norit 17·9 Gr. and in the vessel cooled with liquid air was obtained E : 13·0 Gr. A total of 37 Gr. was recovered; the loss therefore being 3 Gr. In the table below the results obtained, are shown :—

	Bromine number addition	Bromine number substitution.	n_D	Sp. gr. $\frac{18°}{4°}$ C.
A	215·2	9·8	1·3832 (23·1° C.)	0·670 $\left(\frac{19°}{4°}\text{ C.}\right)$
B	149·7	5·0	1·4110 (22·5° C.)	0·738 $\left(\frac{17·5°}{4}\text{ C.}\right)$
C (1·7 Gr.)	212·8	10·0	1·3855 (23·0° C.)	0·673
D	223·6	8·7	1·3817 (22·5° C.)	0·665
E	222·4	9·2	1·3815 (22·5° C.)	0·664

The deviation of this experiment from the results obtained with floridin is the difference in properties of the amylene residue in the porous substance, and thus, in the case of norit, no polymerisation occurs. As with floridin, it can be seen that the bromine numbers of the condensates D and E more nearly approach the theoretical value.

By means of the foregoing experiments, the difference between floridin and norit has been shown. This difference was found again in two experiments in which the vapours of *iso*butylene (Schuckardt) were conveyed through norit and floridin respectively. The theoretical bromine number was 286, but the following results were obtained :— addition : 270 and 275, substitution : 9·8 and 9·2. The values determined differ from the theoretical value, a similar difference usually being found with other olefines (compare communication 1).[4]

[4] This Journal pp. 506-509.

In connection with the low boiling point of *iso*butylene the determination of the bromine number had to be carried out[5] with great precaution, as follows :—

A weighed, sealed tube containing the *iso*butylene was placed in the flask containing a measured volume of the bromine solution previously cooled at low temperature and the tube then broken against the wall of the flask. 3·42 Gr. *iso*butylene was evaporated and the vapours conducted through 4·12 Gr. of the norit kept at ordinary temperature. The evaporation-residue of the *iso*butylene was 0·15 Gr., while in the condenser (cooled with liquid air) was retained 1·84 Gr. of condensate (P). The *iso*butylene-residue in the norit was 1·0 Gr., the loss being about 0·4 Gr. As in the former experiments, the air was previously driven out of the apparatus by means of dry CO_2, but it was proved experimentally that the increase of weight of the norit could not have been caused by the CO_2. The *iso*butylene-residue in the norit was driven out by heating at 160° C. under a high vacuum, and on cooling with liquid air, a condensate was obtained which could be wholly boiled away at ordinary temperature leaving no residue. The decrease in weight of the norit due to this high vacuum distillation was 1·0 Gr. and, by coincidence, this quantity is equal to the increase in the treatment with *iso*butylene. The condensate P obtained on cooling with liquid air, had a bromine number addition : 275·9, substitution : 10·6. It can therefore be concluded that there is no question of polymerisation ; this being quite in opposition to the next experiment in which floridin (5·37 Gr.) instead of norit was used. The floridin was dried by heating at 290°–300°, the decrease in weight on drying being 13·9 per cent. (5·50 Gr. of *iso*butylene were used), and 3·82 Gr. of liquid were collected ; the evaporation-residue was 0·20 Gr., the increase of weight of the floridin was 0·87 Gr., the loss in this experiment therefore being about 0·6 Gr.

The condensate separated by cooling with liquid air, had a bromine number (addition) 276·6 and (substitution) 12·2 and apparently was unaltered *iso*butylene. The floridin with 0·87 Gr. of *iso*butylene-residue was heated for 1½ hours at 170° using a high vacuum. In the glass tube which was placed in the cooled condensation vessel 0·79 Gr. of liquid was separated. This condensate contained in the lower layer, a small quantity of water. The upper layer (the chief part) had an odour quite different from that of *iso*butylene and it did not boil away at ordinary temperature n_D 24° : 1·4350. Bromine number (addition) :

[5] In collaboration with Mr. G. F. de Ridder.

28·7, substitution : 58·0. (The high substitution value obtained with floridin is remarkable.) The low bromine addition proves an important change of the product, but further analytical investigation is necessary in order to prove whether polymerisation has taken place.

In every case these experiments show a great difference in the action of norit and of floridin.

Finally, to illustrate this difference better, the balance of bromine has been considered.

(*a*) Treatment of amylene vapour with dried floridin.

(*b*) The analogous experiment with dried norit.

The result of this consideration is that the norit balance-account is in equilibrium, and there is practically no decrease in unsaturation towards bromine (only 0·3 per cent.) whereas the floridin balance shows a considerable decrease of unsaturation (5·5 per cent).[6]

[6] The evaporation-losses in these experiments are calculated as amylene.

The Composition of Petroleum (Kerosene and other) Fractions, with the Standardization of Miscibility and Optical Tests.

By J. A. Carpenter, M.A., A.I.C.

The present day specification requirements of Motor Spirits and Kerosenes tend towards the presence of aromatic and naphthene hydrocarbons as anti-knock agents in the spirit, together with the avoidance of the same classes of compounds, as far as is economically convenient, in Kerosenes on account of tendency towards smokiness during burning.

While the present work has been in progress, several papers have appeared on similar themes by Mulany and Watson, Waterman and Perquin, Ormandy and Craven and others, but, while nearly all except the first mentioned have dealt with spirits and the application of the Aniline Critical Solution Temperature test to cracked or straight motor fuels, very little reference has been made to the higher fractions.

Most of the work discussed here has arisen directly out of initial trials on the standardisation of the Aniline C.S.T. test for Kerosenes carried out in 1923 and used locally since then; it deals with quantitative and qualitative determinations of aromatics, naphthenes, paraffins and other hydrocarbons in all fractions boiling below 300° C. by C.S.T., Refractive Index, Specific gravity and chemical tests with the aid of fractionation, fractional solution at varying temperatures in solvents such as aniline or o-toluidine, and other physical and chemical means.

The mutual relations of aniline with various classes of hydrocarbons and water yield such an enormous amount of useful information that it is surprising that the solubilities and partitions in the various systems have scarcely been touched upon in work published up-to-date, which has dealt with one or two aspects only in a somewhat empirical manner.

The present work deals with :—

Part I.—The aromatics in petroleum fractions up to 300° C. from a few crude sources.

Part II.—The standardisation of the Aniline C.S.T. method for kerosene fractions.

Further work, some of which has been carried out already and which it is proposed to publish later will deal with the following points, not necessarily in the order given:—

(1) The correlation of the Aniline C.S.T. method with optical and other methods; application to the study of certain crudes.

(2) The physico-chemical study of the liquid systems resulting from aniline and o-toluidine with various classes of hydrocarbon mixtures and with water.

(3) The selectivity for, and separation of, different hydrocarbon classes or individual compounds by various refining methods.

(4) The identification and separation of the non-benzenoid hydrocarbons in petroleum fractions.

(5) The study of fractions above 300° C.

(6) Amplification of any of the above seven points.

The chief crude sources under examination are those from Burmah and Assam, together with a few other sources.

Part I.—The Aromatics in Burmah Crude and other Petroleum Sources.

During the course of work on the application of Tizard and Marshall's Aniline Critical Solution Temperature test,[1] as evolved for spirits, to kerosene fractions, it became necessary to prepare aromatic-free products and at the same time to isolate and identify the aromatics themselves. The aromatic-free products were obtained by repeated extractions with successive quantities of three volumes of 98 per cent. sulphuric acid, while the aromatics themselves were prepared either:—

(1) By Armstrong's method of distilling the first of the sulphonic extracts above with superheated steam,

or (2) by fractional extraction of the suitable fractions with aniline at low temperatures, dissolving out the aniline in dilute acids and redistilling the oily layer after washing.

The second is by far the more convenient method and preserves many substances which become destroyed in the other process. Again, the same principle can be applied to the isolation of other classes of hydrocarbons at other temperatures, depending on the differences of critical solution temperatures and solubilities in aniline (C.S.T. 70° C. upwards for paraffins, 30-65° C. for saturated naphthenes, 10-20° C. for terpenes and well below 0° C. for aromatics).

For example, if it is desired to concentrate on naphthenes, extraction at 30-40° C., after treatment and separation at 0° C.,

[1] *J.S.C.I.*, 1921, **40**, 20r.

will give an extract rich in naphthenes and a residue richer in paraffins.

One extraction is not enough for complete separation of a family of hydrocarbons; it is necessary to repeat the operation on the extract and refractionate the product and so on.

Solubility in aniline is profoundly affected by the presence of water, so that the addition of small quantities of water to a homogeneous mixture some degrees above the C.S.T. has been found to be an added means of fractionation by hydrocarbon class.

In the meantime, Armstrong's method of separation had been also adopted by Mulany and Watson[1] in their study of the aromatics in Burmah spirit and kerosene, and many of their results and those given here are interconfirmatory.

The selection of more or less refined marketed products for these investigations is apt to give misleading results as to the quantity, and even the actual presence of any given aromatic hydrocarbon on account of the fact, either that the product may not be a straight fraction from the crude, or that some substances may have been removed during refining operations.

The Allen Atmospheric system of distillation can be adjusted to concentrate at will on some measure of segregation of desired bodies at worm-ends and a series of adjustments to a distillation bench in 1923 partially illustrates this as follows:—

First adjustment of bench—

Product.	Sp. gr. 60° F.	% Benzene by weight.	% Toluene by weight.	% Xylenes by weight.
Petrol	0·7225 ..	2·1 ..	1·75 ..	nil
Benzine ..	0·7425 ..	7·0 ..	4·1 ..	nil
Naphtha ..	0·7715 ..	nil ..	4·6 ..	6·4
Second adjustment—				
Benzine ..	0·751 ..	4·8 ..	7·5 ..	0·5
Naphtha ..	0·774 ..	nil ..	6·8 ..	7·0
Third adjustment—				
Benzine ..	0·761 ..	1·52 ..	8·5 ..	5·7
Naphtha ..	0·776 ..	nil ..	6·4 ..	3·2

In general, the usual run of spirits from Burmah crude produced normally at the benches, without any further addition of special substances, may be taken to possess aromatic contents by weight as follows:—

	Sp. gr. 60° F.	Benzene.	Toluene.	Xylenes.	Total aromatics.
Special spirit ..	0·717 to 0·722 ..	5·0 ..	3·0 ..	0·5 ..	8·5
Light spirit ..	0·730 to 0·735 ..	4·0 ..	4·5 ..	1·5 ..	10·0
Heavy spirit ..	0·755 to 0·765 ..	2·7 ..	7·8 ..	2·8 ..	13·3

but there is some overlap in the above on account of the fact that heavy spirit is not simply a straight fraction above light spirit

[1] *J.S.C.I.*, 1924, **43**, 310*t*.

but must necessarily contain its correct proportion of lighter constituents.

From the above considerations, the base used in the series below was Burmah crude oil.

This was dephlegmated carefully through a Young and Thomas type 8-section dephlegmator for fractions up to 150° C. and a 3-section for higher fractions. A small amount of cracking occurs when the temperature is over 200° C., so that in most of the distillations, open steam was introduced after the still head temperature had reached 180° C. and the dephlegmator had been removed.

The resulting fractions were afterwards fractionated by dry-distillation and cut to narrow boiling point ranges.

With an American petroleum source, it was necessary for qualitative examination of the nature of the aromatics and use of these in developing the C.S.T. test, to use a marketed refined kerosene which had already lost some proportion of its aromatics in refining.

Burmah Crude.

The crude was dephlegmated into 5° C. cuts but in the series described below, slumped cuts of these were taken at 125° C., 150° C., 180° C., 210° C., 230° C., 250° C., 270° C. or 275° C. and 300° C.

In the first series, using Armstrong's method, each cut was treated separately from the others with three volumes of 98 per cent. sulphuric acid for half-an-hour. The acid tar was separated and subsequently distilled with superheated steam to recover the aromatics.

In another series the whole distillate was treated as one fraction and the recovered aromatics were fractionated subsequently. It was recognised in the first series that the presence of constant boiling mixtures, formed between aromatics and aliphatics, would bring some aromatics into their wrong b.pt. limits, but this was not found to be a serious drawback in analysis.

The various fractions of aromatics thus obtained were examined by several methods, *e.g.*, poly-nitration (by Mulliken's method, also by Dr. Watson's method communicated by him in 1921, and afterwards published in his paper,[2] oxidation, picrate formation, analysis of barium sulphonates, etc. The total amount of aromatics recovered by Armstrong's method was approximately 60 per cent. of the theoretical yield estimated by all the methods available (loss in acid, aniline point methods, etc.).

The original untreated crude fractions were also examined for the possible presence of substances likely to be changed or destroyed by the acid treatment (*e.g.*, terpenes, heterocyclic bodies).

One typical analysis resulted as follows:—

Fraction.	% by vol. on crude.	Sp. gr. 60° F. Aromatic free portion.	Sp. gr. 60° F. Aromatics.	% Aromatics on cut by vol.	% on crude by volume. Non-arom.	Aromatics
Under 125° C. ..	16·00	0·7266	0·871	11·5	14·15	1·85
125—150° C. ..	6·61	0·7600	0·866	18·3	5·40	1·21
150—180° C. ..	5·42	0·7730	0·872	19·9	4·34	1·08
180—210° C. ..	4·80	0·785	0·888	18·5	3·91	0·89
210—230° C. ..	4·85	0·797	0·910	18·1	3·97	0·88
230—250° C. ..	4·68	0·805	0·930	19·4	3·77	0·91
250—275° C. ..	7·14	0·812	0·945	24·2	5·41	1·73

The aromatic contents given above are the calculated totals. Above 290° C., the content rises very markedly, partly due to cracking in the distillations as carried out, and partly due to the presence of many aromatic and kindred bodies, saturated, unsaturated and polymerised, which occur with a boiling point near 300° C. and over (see later).

The detailed analyses are subject to fluctuation with variations in the crude from time to time, but there is always a maximum aromatic content in the range about 140-190° C., corresponding to xylenes and cymene, also cumene, mesitylene and pseudocumene. Thereafter a minimum occurs about 210-220° C., and above that there is a rapid rise in content corresponding to naphthalene derivatives and certain condensed bodies based on the 5-ring cyclo-pentadiene nucleus with their polymerisation products.

Fractions under 125° C.

The presence of benzene and toluene has been confirmed quantitatively so often and by so many means that no doubt exists about them. The aromatic content in Yenangyoung crude under 125° C. is somewhat higher than that in the corresponding fraction from Singu, but average figures for dephlegmated mixed crude from the two fields, cut at 95° C., 125° C. and 150° C. are as follows:—

Fraction.	Sp. gr. 60° F. of cut.	% Cut on crude.	% Aromatic on cut by vol.	% Aromatic on crude by vol.	Nature.
Under 95° C. ..	0·712 to 0·714	6·0	9·5	0·57	Benzene
95—125° C. ..	0·756 to 0·758	10·0	13·5	1·35	Toluene
125—150° C. ..	0·773 to 0·776	6·5 to 6·7	18·0	1·15 to 1·21	Xylenes

The toluene yields T.N.T. (M.Pt. 82° C.) quantitatively by Watson's method.

Fraction 125-150° C. (Aromatic fraction).

Nitration.—This was polynitrated and gave a crystalline mass fractionating from hot alcohol into fractions melting from 130° C. to 230° C., the bulk being at 178-183° C. On repetition with other similar aromatic fractions, the initial melting point was lowered to 100° C., and these first fractions showed evidence of very small amounts of toluene and ethyl benzene, confirmed by a smell of benzoic acid on oxidation of the original with CrO_3 or alkaline permanganate and acidification.

The next T.N. fraction showed a vague melting point at 140° C., while the two following ones melted sharply at 180° C. and 230° C. respectively. T.N. p-xylene melts at 139° C., but is not easy to prepare, T. N. o-xylene and T.N.m-xylene have melting points 178° C. and 182° C. respectively, T.N. mesitylene at 232° C. Mesitylene boils at 164° C., and the definite presence of small quantities here is due either to the presence of constant boiling mixtures in the original kerosene or to imperfect fractionation.

Oxidation.—Oxidation with aqueous alkaline permanganate gave a good yield of crystalline substance melting above 280° C., indicating phthalic acids.

The dimethyl ester was prepared as given in Mulliken Vol. I, page 85, and the product, precipitated by water from methyl alcohol solution, was recrystallised from dilute methyl alcohol, giving fractions at 62° C. (vague) and 139° C. (sharp), thus indicating the presence of Iso- and Terephthalic acids respectively (M.Pt. esters 64° C. and 140° C.).

o-Phthalic acid was indicated by obtaining a fluorescein test after heating with resorcin and zinc chloride.

Though ethyl-benzene in the presence of excess of xylenes is difficult to identify with certainty, some fractionations of the aromatics give distinct indications of a compound boiling at 135° C., though this is not reliable on account of the proximity of the various boiling points.

From a combined study of the fractions, nitration and oxidation products, the following analysis is probably a fair estimate :—

Substance.	B.pt. °C.	% on fraction.	% on crude by vol.
o-Xylene	143	15	0·17
m-Xylene	139	60	0·73
p-Xylene	138	20	0·24
Ethyl benzene	135	2	0·03
Mesitylene	164	3	0·04
	Total	..	1·21

Though present only in quantities of the order of 0·1 per cent. in 140-150° C. fractions of a carefully distilled crude, Styrene,

$C_6H_5{\cdot}CH{:}CH_2$, B.Pt. 144° C., is present in greater quantities in cracked kerosene. Evidence on which the presence of styrene rests is:—

(1) A bromine value of 1·6 per cent. for the 140·150° C. fraction.
(2) When the acid tar from the fraction is distilled with steam, the resulting distillate on fractionation gives a small quantity of an oily body boiling near 310° C.
(3) After exposing the same fraction to sunlight for a few days in the case of a cracked kerosene (though not in carefully distilled kerosenes) a similar oily residue remains on distilling to 300° C.; this boils with partial decomposition between 300 and 320° C. and consists mainly of Xylylstyrene, $C_{16}H_{18}$, together with unsaturated constituents (mainly stilbene or homologues). This residue oxidises in the air and gives an odour of benzoic acid on oxidation with chromic acid mixture.

The probable role of xylene in condensation and oxidation reactions under the influence of sunlight will be discussed below after considering other fractions in detail.

Fraction 150-180° C.

The simple aromatics to be expected in this range are included among:—

	B.pt. ° C.
Cumene (isopropyl benzene)	153
n-Propyl benzene	158
Tert. butyl benzene	167
Mesitylene (1.3.5. trimethyl benzene)	164
Ethyl toluenes	161—165
Pseudo-cumene (1.2.4 trimethyl benzene) ..	169·5
Hemimellithene (1.2.3 trimethyl benzene) ..	175
p-Cymene (1-methyl-4-isopropyl benzene) ..	175

together with terpenes and small quantities of higher boiling substances.

A study of the paraffin hydrocarbons in early Burmah fractions shows that high proportions of branching chain hydrocarbons are present in which several small alkyl groups branch off nuclear carbon atoms rather than form long chains.

On this analogy, it is probable that the aromatics will show the same main tendency, *i.e.*, that small alkyl groups will be closely attached to the nucleus rather than form single long side chains. If side chains of any magnitude are formed then it is probable that these will be iso and tertiary alkyls rather than normal groups. This view is confirmed in fair measure by the chemical data obtained below.

Nitration.—Polynitration gave a mixture of pale yellow crystals melting between 102 and 232° C. On repeated refractionation from alcohol, acetone and acetic acid, the fractions became colourless, and were :—

M.pt. 106–7° C. —2.4.6. T.N. cumene melts at 109° C.
120° C. approx.—T.N. *p*-cymene melts at 119° C. (?) and 4.5.6. T.N. *m*-xylene melts at 125° C.
178° C.— —T. N. pseudo cumene melts at 185° C.
182° C.— (Possibly some xylenes are also present.)
230—232° C. —T.N. mesitylene melts at 232° C.

No nitro compound of m-Cymene (M.Pt. 73° C.) could be traced.

A strong odour of musk suggested the presence of tertiary-butyl benzene.

The main fractions above were those at 106° C. and 178-182° C. Ultimate analysis of the nitrogen content gave N=16·50 to 16·57 per cent. (C_9H_{12} requires N=16·47 per cent.) for the 182° C. and the 232° C. fractions, while those at 120° C. and 178° C. indicated a lower percentage favouring a formula nearer to $C_{10}H_{14}$ (M.Wt. found 264, T.N. Cymene requires 269).

A further narrow fraction of the original aromatics redistilled to 165-172° C. gave two T.N. derivatives melting at 160° and 186° C., the latter being pure T.N. pseudo-cumene, while a narrow cut boiling in the immediate neighbourhood of 175° C., (at which point a large proportion of hydrocarbons distils) made from aniline extracted sources, gave two crops of T.N. derivative melting at 163° C. and 178° C.

The hydrocarbon at this point gave an analysis of $C_{10}H_{14}$ with a dimethyl ester of terephthalic acid melting at 140° C. on the necessary oxidation and methylation treatment. Mulany and Watson give 180° C. as the melting point of T.N. p-Cymene, while other references give 119° C. These discrepancies have not been cleared up, but the fact nevertheless remains with certainty that a large quantity of p-Cymene is present.

Further preparations and recrystallisations of similar fractions yielded also T.N. fractions near 90° C. and 210° C. rather indefinitely. These indicate small quantities of p-Ethyl Toluene (T.N. M.Pt. 92° C.) and Hemimellithene (T.N. M.Pt. 209° C.).

Barium Sulphonates.—These were prepared from the aromatic fraction by treating with one volume 98 per cent. sulphuric acid at 100° C. for three hours and neutralising with Barium carbonate.

Three crops from water yielded :—

(1) Ba=25·2% (cumene Ba-monosulphonate requires 25·6% Ba).
(2) Ba=24·6% (cymene deriv. requires 24·47% Ba).
(3) Ba=24·95%.

Oxidation.—Alkaline permanganate oxidation gave benzoic and phthalic acid crystals melting over 290° C., o- and p- phthalic acids were well indicated, but no methyl ester of isophthalic acid could be obtained.

Terpenes.—This is the fraction in which terpenes if present should show themselves, particularly as p-Cymene is present in quantity.

Terpenes can be tested for roughly by aniline point differences between 80 per cent. acid-treated and untreated fractions, a difference of 0·3° C. on the average being produced by 1 per cent. terpene added to an aromatic-free kerosene. The terpenes are not entirely soluble in 80 per cent. acid,though if present in small quantity, they are dissolved out completely by 85 per cent. acid, With 150°-180° C. fractions of original kerosene, such aniline point differences using 80 per cent. acid varied from 0·2° C. to 0·6° C., while bromine absorption values varied from 0·4 to 1·0 per cent. A 150-180° C. fraction extracted with aniline at 20° C. (after previous extraction of aromatics at -16° C.) gave an approximate content of 8 per cent. of terpenes in a 10 per cent. extract from the original fraction, hence all these data go to show that true terpenes are present in extent not exceeding 1 per cent. to 2 per cent. on the original 150-180° C. kerosene fraction, and therefore 0·05 to 0·11 per cent. on the crude.

Optical activity is not noticeable in these fractions.

From the fractionation results, combined with other observations on nitro and oxidation derivatives, it can be deduced that cymene and cumene are present in greatest quantity with pseudocumene a good third and mesitylene fourth, so that a rough estimate is as follows :—

Substance.	B.pt. °C.	% on Aromatic fraction.	% on crude by vol.
Cumene	153 ..	25 ..	0·27
Mesitylene	164 ..	14 ..	0·15
Pseudocumene ..	169·5 ..	20 ..	0·22
Hemimellithene ..	175 ..	8 ..	0·09
p-Cymene	175 ..	27 ..	0·29
Tert. butyl benzene..	167 ..	3(?) ..	0·03
Ethyl toluenes ..	161–5 ..	3 ..	0·03
		Total ..	1·08

Add—Terpenes in original fraction, say 0·08 per cent. on crude.

Fraction 180-210° C.

It is at this stage that points of very great interest arise Fractions above 180° C., or those with an F.B.P. at 190° C. or above, begin rather suddenly to show the property of colour

reversion unless carefully refined, and even then they are oxidised and coloured under the action of bright sunlight.

These distillates also begin to exhibit fluorescence in increasing degree. It has been demonstrated beyond question that bodies other than paraffins, naphthenes and true aromatics are present and that some of these are bodies allied to indene, fluorene and the fulvenes, *i.e.*, five-carbon rings condensed with benzene nuclei.

They are derivatives of cyclo pentadiene, the single ring compounds of which appear to exist in cracked spirits and light kerosene fractions, but not in uncracked straight fractions. This class of bodies does not appear in the aromatics as prepared by Armstrong's method, owing to resinification, but aniline extraction preserves them. A discussion of their properties and modes of production is deferred until the true aromatics have been considered.

The true aromatics to be expected in this range may be as follows :—

	B.pt. ° C.		B.pt. ° C.
Cymene	175	Isopropyl *m*-xylene ..	194
Butyl benzene	180	Durene (1, 2, 4, 5 tetram.)	194
Diethyl benzenes ..	182–3	Isodurene (1, 2, 3, 5 „)	196
Propyl toluenes ..	182–3	Prehnitine (1, 2, 3, 4 „)	204
Dimethyl ethyl benzenes (or ethyl xylenes)	183–5	Diethyl toluenes	200
		Tertiary butyl toluene ..	200
Isobutyl toluenes ..	187—197	Ethyl butyl benzenes ..	200–5
Tertiary amyl benzene ..	187	Diisopropyl benzenes (*m* and *p*) ..	202–4
Isoamyl benzene ..	193		

and many of formulae $C_{11}H_{16}$ and $C_{12}H_{18}$, with different alkyl groups and arrangements, boiling at 206-220° C.

There is a very great number of possibilities and probably that is why the fraction is difficult to deal with.

From what has been said already, it is probable that if the larger alkyl groups are attached to the benzene nucleus, they will form mono- or di- substituted isopropyl, iso- and tertiary- butyl, iso-amyl and such like derivatives, rather than the normal chain homologues. Otherwise, the smaller alkyl groups will be joined directly to the nucleus, giving the durenes, diethyl benzenes, isopropyl xylenes, etc.

Some poly-substituted bodies cannot form trinitro derivatives, but a well crystallised T.N. mass was obtained from the aromatic fraction boiling between 180 and 210° C., extracted by aniline.

This T.N. mass melted over the range 107-120° C. and smelt very strongly of musk (T.N. tertiary butyl toluene); attempts at further fractionation gave crystals melting at 196° C., 190-192° C., 168-170° C. and 100-125° C.

Possibilities :—

	M.pt. ° C.
T.N. tert. butyl toluene	97
T.N. ethyl *m*-xylene	127
T.N. ethyl *p*-xylene	129
T.N. isopropyl *p*-xylene	195
T.N. *m*-diisopropyl benzene	111
T.N. Tert. butyl *m*-xylene	182
Dinitro tetraethyl benzene	115
Dinitro tetramethyl benzenes	156, 178, 205

As complete tables of nitro derivatives are not available and ultimate analysis does not help to distinguish between the possibilities, the subject is left here for future work.

Oxidation with alkaline permanganate yielded a mass of crystals on acidifying the reaction solution after filtration from oxides of manganese.

The precipitated acids were easily identified as benzoic and the phthalic acids by the usual tests, but evaporation of the acidified solution to dryness gave a mass which melted away from the potassium chloride at 240° C. The melt dissolved easily in water, and was recrystallised, giving an acid mixture melting at 235-242° C. Combustion gave inconsistent results owing to the presence of water until the mass had been well heated almost to fusion, when the result was C 47·45 per cent. H 2·41 per cent. O 50·14 per cent.; $C_{10}H_8O_8$ requires C 47·24 per cent. H 2·36 per cent. O 50·40 per cent.

Hence, the substance was mostly Mellophanic acid derived from Isodurene (1, 2, 3, 5 tetramethyl benzene).

The trouble in drying suggests that Prehnitic acid, crystallising from water with $2H_2O$, was also present, this being derived from Prehnitine, 1, 2, 3, 4 tetramethyl benzene (Mellophanic acid, M.Pt. 238° C., Prehnitic acid about 240° C.). The fused acid gave off water on heating with formation of anhydrides. Possibly Pyromellitic acid (from Durene) was present, though the melting point of the latter acid is 264° C. The presence of benzoic acid suggests the presence of monoalkyl benzene derivatives, probably one or more of the iso- or tertiary butyl or amyl-benzenes, while the phthalic acids confirm that di- derivatives (tert. butyl toluene, di-isopropyl benzene, possibly some cymene, butyl toluenes, etc.) are present in fair quantity.

Further identifications are not a matter of much importance, but it is probable that several, if not most, of the compounds given in the list are present with definitely traced hydrocarbons such as :—

Isobutyl or Isoamyl-benzene.

Di-derivatives of benzene, $C_{10}H_{14}$ and $C_{11}H_{16}$.

Tertiary butyl toluene.
Isopropyl xylenes.
Isodurene and Prehnitine.

Actual fractionation of the aromatic 180-210° C. fraction obtained by means of aniline extraction gave :—

°C.	%	°C.	%
180—182 ..	19·0 ..	192—195 ..	1·4
182—189 ..	27·2 ..	195—200 ..	25·2
189—192 ..	11·2 ..	200—210 ..	16·0

Fractions 210° C. and Upwards.

The predominant features in the higher ranges are :—

(1) Gradually increasing yellow colour of the aromatic distillate with ascending boiling point.
(2) The absence of well-defined nitro derivatives on attempted polynitration.
(3) The production of phthalic acids with naphthoic acids at times on oxidation.
(4) The easy production of well-defined picrates by boiling with picric acid in alcohol solution and recrystallising the product from alcohol or toluene. The colour of these picrates gradually increases from yellow to deep red through deep orange on ascending the series.
(5) The sudden increase of specific gravity in this range.

The aromatics in this range are therefore mainly naphthalene derivatives, with some measure of the higher benzene homologues such as Diisobutyl benzene (230° C.), Tetraethyl benzenes (250° C.), Hexamethyl benzene (264° C.), Diisoamyl-benzene (265° C.), Pentaethyl benzene (277° C.) and others including phenyl methane derivatives.

Very vague results were obtained from preliminary experiments similar to those described for lower fractions. Picrates from the whole range, however, gave a large yield which fractionated at 70° C., 90° C., 105-110° C., 114-115° C., 122° C., 133-139° C. Above 295° C., the main result was a blood-red picrate melting at 79-82° C. identified as that of γ-methylene diphenylene, an isomer of fluorene, while fractions over 300° C. gave a picrate of m.pt. 83-86° C.

From the gradually increasing intensity of colour throughout the fractions when treated separately, it appears that the substances producing the blood-red picrates are in gradually increasing quantity. This is also in accord with the fact that aromatic content in the original kerosene fractions also increases gradually from 220° C. upwards even under careful distillation, but more rapidly when cracking is allowed to take place.

The picrate fractionation results may represent the following :—

Substance.	Picrate m. pt. ° C.	Hydrocarbon b. pt. ° C.
β-Ethyl naphthalene.. ..	70 ..	251
β-Isopropyl naphthalene ..	89 ..	265—275
α-Isoamyl	85—90 ..	290
α-Ethyl naphthalene.. ..	98 ..	258 (decomposes partially)
β-Isobutyl naphthalene ..	96 ..	280
β-Isoamyl naphthalene ..	110 ..	290
α- and β-methyl naphthalene	114—117	240—242
1-6-Dimethyl naphthalene ..	114 ..	262–5
Trimethyl naphthalene ..	133 ..	275
1-4 Dimethyl naphthalene ..	139 ..	262–4
Amyl naphthalene	141 ..	305
Unchanged picric acid ..	122 ..	—

Naphthalene itself (picrate 150° C., boiling point 218° C.), if present at all, can only occur in minute quantities.

It was impossible to crystallise naphthalene from the 215-220° C. fraction, and picration gave only a minute yield melting at 150° C. after the main fraction had melted at 133-139° C.

The aromatic fraction 230-250° C. yielded crops of picrates melting at 98° C., 105-110° C. and 115° C.

Barium sulphonates were prepared and yielded amorphous masses from water in crops giving :—

		%			%
First crop	Ba =	21·9	Fourth crop	Ba =	18·7
Second crop	Ba =	21·8	Fifth crop	Ba =	19·6
Third crop	Ba =	19·1			

Assuming that at 100° C., one volume of 98 per cent. H_2SO_4 gives the monosulphonic acid, percentages of Ba in methyl, ethyl or dimethyl, and amyl naphthalenes will give 23·8 per cent., 22·7 per cent. and 19·95 per cent. Ba respectively. Molecular weights in benzol gave subnormal results, while combustions of narrow fractions gave variable results, and oxidations, carried out mildly, yielded substances corresponding to α-naphthoic acid (M.P. 160° C.) and β-naphthoic acid (M.P. 182° C.) together with *o*- and *p*- phthalic acids.

The persistent presence of terephthalic acid in the oxidation products of these fractions indicates that such benzene derivatives as *p*-di-isobutyl benzene (230° C.) and *p*-di-isoamyl benzene (265° C.) are present, and it is probable that the penta and hexa alkyl derivatives are included; this possibly explains Mulany and Watson's observation that a certain fractionated aromatic hydrocarbon did not seem to be as pure as the barium sulphonate made from it in the identification of β-isoamyl naphthalene.

The writer did not confirm that large quantities of this hydrocarbon existed to the exclusion of others, such as the isobutyl and isopropyl derivatives of naphthalene, but in order to investigate the matter more closely, the aromatics extracted by means of aniline from the kerosene (215-300° C. fraction) were dephlegmated carefully and examined in narrow cuts with the results given in the table below.

NOTE.—A = Picrate recrystallised from alcohol.
T = Picrate recrystallised from toluene.

Picrates gradually increased in colour from yellow through orange to blood-red as the fractions ascended. Repeated recrystallisation of picrates from the upper fractions, however, yielded an orange product of higher and a deep red product of lower melting point. The hydrocarbons themselves became increasingly yellow as the series was ascended.

Where two or more ranges of melting point are given, these were obtained by fractional crystallisation.

Yields were very good, particularly in the case of the larger fractions:—

Fraction. ° C.	Amount. % by vol.	Picrate m. pt., ° C.	Remarks.
215—220	7·7	103—105 A	Yellow picrates.
		129—133 A, 137 T	Indication of a trace at 150° C.
220—225	3·2	115—125	
225—230	5·0		
230—238	6·4	96—98 A	
		101—103 A	
		96—97 T	
238—245	12·8	96—99 A	
		108—110 A	
		96—103 T	
245—248	4·5	108—112 A	
248—255	12·3	95—98 A, 105—108 A	Orange yellow picrate
		95—105 T	
255—260	2·7	96—105 A	
260—267	9·8	96—100 A	
		102—108 A	
		102—106 T	
267—275	10·7	102—108 A	Deep red picrate.
		88—98 T	
275—280	6·8	105—110 A, T	
280—290	6·4	95—102 A	
		101—105 T	
290—300	4·1	103—113 A, T	Orange.
		79—82 A, T	Deep red.
300—320	4·0	103—110 A	
		83—86 A	
Over 300	3·6	—	

Fractions over 300° C. were of a deep yellow colour, of sp.gr. 1·024 at 60° F.; they oxidised rapidly in air, and their unsatura-

tion values varied from 10 to 20 per cent. (bromine value). These fractions decomposed partially on distillation with formation of resinous residues (see later) and contained small quantities of phenolic bodies.

Nitration of these fractions simply yielded dark, sticky masses of low melting point (*e.g.*, 230-238° C. fraction, M.P. 60-66° C., and 260-267° C. fraction, M.P. 70-75° C.).

The predominance of the range of picrates melting between 95-100° C. and 105-110° C., with some slightly above this, shows the presence of the methyl, ethyl, isopropyl, isobutyl and isoamyl derivatives, both α- and β-, but fractionation must be drastic before any good separation can be effected, either by boiling or through the derivatives.

Considering that the main constituents are now known with reasonable certainty, lack of time and other considerations have so far prevented the completion of the study by means of determining complete series of combustion analyses, molecular weights and other data for narrow fractions.

An American Kerosene (Elephant Brand).

The object in examining aromatics from this source was simply to see how they affected the Aniline C.S.T. when isolated and used synthetically, so that the attention given to them was not as detailed as for Burmah products.

The aromatics, comprising some 10-12 per cent. of the bulk of the kerosene, were isolated by the methods already described, and were found by similar methods of analysis to contain many of the same constituents as those in Burmah crude. Considering that the product examined was a refined marketed kerosene, no notice can be taken of the quantitative side.

A distillation of the complete range of extracted aromatics gave the following tabulated results:—

Fraction. ° C.	Amount. % by vol.	T.N. deriv. m. pt., ° C.	Picrate. m. pt., ° C.	Remarks.
143—172 ..	9·3			
172—177 ..	6·2	105—125 ..	—	
177—195 ..	11·4			
195—210 ..	15·1	110—112 ..	85—108	
210—225 ..	10·8	—	98—112	
225—240 ..	11·4	—		
240—250 ..	11·7	—	98—107	
250—260 ..	6·8	—		
260—280 ..	8·4	81—98 ..	98—107	
280—300 ..	8·4	— ..	105—111	

The T.N. derivatives of the lower fractions gave higher melting constituents on fractionation up to 185° C.

The low end of the kerosene is too high for most of the xylenes, but contains cumene, ethyl toluenes, cymene, practically no terpenes, some pseudo cumene and several representatives of polymethyl- and ethyl- derivatives of benzene, such as ethyl xylenes, durenes, tetraethyl benzenes, &c. Oxidation gives the usual phthalic and other acids.

The upper end gives crystallisable nitro bodies corresponding to the benzene derivatives more easily than in the case of Burmah fractions, but the usual substituted naphthalenes of much the same type are also present to some extent, picrates showing methyl-, ethyl-, propyl-, iso-propyl- and amyl naphthalenes.

The aromatic fractions near 300° C. are yellow and unstable, turning dark with oxidation and behaving just like their Burmah counterparts.

On the whole, it appears that the aromatics are not much different in type from those contained in Burmah oil, except that the naphthalene derivatives are in lower proportion.

Badarpur Crude Fractions.

A fraction representing 26·5 per cent. on the crude after the first 5 per cent. had been removed as spirit, gave the following results on distillation by the A.S.T.M. method :—

Sp. gr., 60° F.			0·893		
I.B.P.			102° C.		
F.B.P.			348° C.		
Under 125° C. ..	0·5%	Under 250° C. ..		61·0%	
150	3·5	275		82·0	
175	12·5	300		92·5	
200	27·0	325		97·0	
225	42·5				

On fractionation into narrow cuts, the aromatic content rose gradually from about 7 per cent. in lower fractions to over 50 per cent. in fractions near 300° C. As a whole, the fraction gave :—

	Sp. gr., 60° F.	Aniline pt., °C.	Loss in 98% acid. %
Original	0·893	28·0	—
After 80% acid	0·8946	29·2	4
After 98% acid	0·8526	59·6	38

Extracted aromatics gave sp. gr. 60° F.=0·93 to 0·95.

Thus, true terpenes amounted to about 4 per cent., along with about 35 per cent. of aromatics, while the aromatic-free portion after drastic acid treatment smelt very strongly terpenic, and after exposure to sun and air, somewhat camphoric.

Unsaturation values were slightly higher than those for Burmah fractions.

In order to test whether the formation of aromatics or terpenes proceeded progressively by cracking under ordinary distillation, the aromatic-free portion was redistilled from an Engler flask and the fractions tested for aniline points before and after strong acid treatment.

Results:—

Fraction. °C.	Sp. gr. 60° F.	An. pt.	An. pt. after 80% acid.	An. pt. after 98% acid.
165—210 ..	0·8398 ..	58·5 ..	58·8 ..	59·2
210—230 ..	0·8582 ..	59·8 ..	59·8 ..	60·2
230—250 ..	0·875 ..	61·4 ..	61·6 ..	62·4
250—270 ..	0·8865 ..	63·4 ..	63·4 ..	63·4
270—300 ..	0·900 ..	65·2 ..	65·2 ..	67·6
Over 300 ..	0·926 ..	66·5 ..	66·7 ..	74·8

These differences are higher than those obtained from Burmah aromatic-free fractions under similar circumstances; sunlight also acts on Badarpur aromatic-free fractions with formation of colour much more readily than on Burmah or American fractions. Hence it is possible that the enormous content of aromatics in later fractions is partly due to cracking of the curious naphthenic portion, which seems to consist partially of fully hydrogenated members of terpenic and naphthalenic families.

Badarpur aromatics were extracted from the kerosene and dephlegmated into narrow cuts. The chief maxima were around 140-145° C., 170-175° C., 190-195° C., 205-210° C., 215-220° C., 240° C., 245-248° C., 258-264° C., 270-275° C., 290-300° C., 322-325° C., with I.B.P. at 95° C. and F.B.P. with a residue at 370° C.

The amount below 150° C. was 6·8 per cent., 150-200° C. 13·3 per cent., 200-275° C. 50 per cent., 275-300° C. 13·4 per cent., so that the greater portion consisted of naphthalene derivatives, the picrates of which nearly all came in the melting point range 95° to 110° C.

Trinitro derivatives were prepared from lower fractions, those from:—

Fraction	145—160° C.	were of m. pt.	142—154° C.
„	165—177° C.	„ „	120—136° C.
„	177—200° C.	„ „	125—140° C.

These gave higher and lower fractions on recrystallisation, but higher fractions would only give brown amorphous masses by the polynitration method.

Toluene, xylenes, mesitylene, cumene, cymene, tri- and tetramethyl benzenes, naphthalene, methyl-, ethyl-, isopropyl-, isobutyl-

and isoamyl naphthalene (and phenyl naphthalenes above 300° C.) are present, but exhaustive enquiry has not yet been made, the main object so far having been to use these aromatics in the development of the aniline C.S.T. test. On the whole, Badarpur aromatics are qualitatively similar to those in Burmah crude, even to the tendency towards the formation of branching chain alkyl derivatives, though quantitatively the heavier bodies are in much greater proportion. The heavy aromatic ends again exhibit the same deep yellow, red and brown colours; they are unstable with the property of turning dark in air with oxidation and partial resinification.

The further detailed study of Badarpur crude will not be given in this paper except for a few notes in Part II.

Unstable Compounds in Kerosene Fractions.

From 180° C. upwards, untreated kerosene fractions begin to exhibit the phenomenon of fluorescence in increasing degree together with a tendency to revert in the dark and in bright sunlight to a yellow colour. During the course of researches on the colour reversion of kerosene mainly from Burmah but also from other sources, a few salient facts have been noted as follows :—

(1) An untreated kerosene will revert in the dark to high yellow tints, but the liquid remains clear.

(2) A sufficiently acid-treated or filtered kerosene (bauxite, fuller's earth, etc.) will not revert in the dark.

(3) Whether treated or untreated, filtered or unfiltered, the same kerosenes will revert strongly in sunlight with oxidation. The colour first turns to yellow, later on cloudiness appears, and then resinous bodies of a reddish colour become deposited, together with a powdery yellow solid which, on exposure to air, turns dark with rapid oxidation.

(4) Kerosenes which revert in either dark or sunlight do not revert as quickly in diffused light.

(5) A dark-reverted kerosene bleaches in sunlight to a perfectly clear (though possibly tinted) solution at first with no trace of precipitation, but this proceeds to revert in sunlight at the same rate as any other kerosene, and sometimes very rapidly.

(6) Reversion is to some extent catalytic, the presence of reverted bodies accelerating the action on the remainder.

(7) Kerosenes from which the aromatics and unsaturateds have been removed by drastic treatment still revert slightly and very slowly in bright sunlight in air, but not in atmospheres of carbon dioxide and nitrogen.

(8) On distilling a dark-reverted kerosene, a small non-volatile residue of an orange colour and sticky nature is produced. This, on solution in benzol and oxidation, yields a dark hard resin after evaporation of the solvent.

(9) On distilling a sunlight-reverted kerosene, a large quantity (5 up to 10 per cent.) of a dark non-volatile resin is left. This is unsaturated, contains nearly 30 per cent. of oxygen, and is strongly reminiscent of bodies allied to di-cyclopentadiene diperoxide, and to the oxidation products obtained from *p*-xylene in sunlight.

(10) Sunlight reversion is non-reversible.

(11) When the final boiling point of a cut is below 185-190° C., no appreciable reversion occurs either in the dark or in sunlight unless the fraction has been intentionally cracked. Above this limit there is a very marked and sudden effect, particularly in sunlight.

(12) Acid treatment of the sunlight-produced resins yield tarry matters, which, when reasonably free from acid (a matter of difficulty to secure), give distillates containing cresols soluble in alkalies, the residues yielding at times hard, and at times soft, resins by extraction with organic solvents and evaporation. Acid tar from dark-reverted resins gives similar effects, but the resultant products are not as rich in oxygen as the others.

(13) Kerosenes with a final boiling point below 290° C. are far more easily filtered for removal of colour than those above this range, though, if untreated, the F.B.P. rises above this limit spontaneously on standing owing to the formation of polymerised and oxidised substances. This 290° C. limit is extremely well marked, and the reasons for it will appear later.

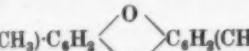
(14) The smells of the various resins and residues are characteristic, varying from terpenic in dark-reversion, to penetrating odours, sometimes resembling burnt toffee, in other cases.

The observations show that dark-reversion is due to condensation or polymerisation of bodies already present adventitiously in moderately small quantities, and that little or no oxidation is necessary to bring it about.

The bodies causing this reversion are easily removed. Diffused light is not sufficient to promote oxidation but it has a tendency to inhibit polymerisation of existing unstable compounds. Sunlight reversion is a more fundamental change and, though a small amount of reversion is possible in the absence of air, the main action is one of oxidation, followed by condensation and polymerisation. This affects a considerable proportion of the oil. Precisely the same effects have been obtained with American refined kerosenes of the highest grades as well as with those from Asiatic sources.

In a few cases, the intermediate formation of aldehydes has been suspected but not proved.

Very little rise in acid value is noticed and the main coloured substances produced are akin to polynuclear fulvene derivatives (possibly due to condensation of aldehydes with indene and fluorene derivatives), also to coumarone derivatives and especially to peroxides of unsaturated ring compounds or oxidised condensation products from xylene, mesitylene, etc., such as



$(CH_3)\cdot C_6H_2 \begin{matrix} O \\ \diagup \quad \diagdown \\ O \end{matrix} C_6H_2(CH_3)_2$. The solid yellowish product, not unlike flowers of sulphur in appearance, which sometimes deposits from a sunlight-reverted kerosene on long standing, is very unstable. It absorbs oxygen at once when exposed to the air, at the same time turning dark and tending to melt. Combustion analysis gives variable results from $(C_4H_3O_x)_n$ to $(CHO_x)_n$ and $(C_3H_4O_x)_n$ according to conditions and the amount of oxygen absorbed. The substance in one case was thought to be a substituted di cyclopentadiene peroxide, while another such body was produced quickly from a 295-300° C. fraction and was probably a peroxide of phenyl-fluorene, as oxidation gave evidence of a mixture of phthalic and benzoic acids.

The partially heated resins produced on reversion, or as residues on distilling a reverted oil, give high degrees of fluorescence when their sulphonates are poured into alkali solutions.

The behaviour of the yellow kerosenes on bleaching in sunlight is strongly reminiscent of several well-known changes such as :-

(1) The behaviour of anthracene in xylene solution. (Reversible change in sunlight to dianthracene with clouding of the solution.)

(2) The behaviour of certain unsaturated ketones, *e.g.*, dibenzoyl ethylene, $C_6H_5\cdot CO\cdot CH{:}CH\cdot CO\cdot C_6H_5$, which exists in a

coloured and a colourless form, changed from one to the other in sunlight or on heating.

(3) Colour changes of bodies with certain "quinoid" double bond arrangements as in quinones, fulvenes and in bodies possessing wandering and reactive hydrogen atoms.

(4) The properties of indene, C_9H_8, with its homologues. These turn yellow on standing and bleach in sunlight, afterwards forming resins on standing.

The same is true of several bodies known in coal-tar chemistry.

In order to examine the matter further, fractions of the original untreated kerosene obtained from Burmah crude, boiling at 170-200° C., 200-250° C., 280-300° C. and 170-300° C. were treated as follows:—

(1) With half their volume of 98 per cent. sulphuric acid.

(2) With metallic sodium at 120° C. for six hours, either in the presence of a stream of dry ammonia gas or of a drop of aniline.

(3) Under a reflux condenser at 180-200° C. in the presence of solid caustic soda for several hours, agitating with a current of air. The temperature was carried as high as the kerosene permitted, without boiling.

(4) By filtration through bauxite, afterwards washing the bauxite with petroleum spirit and then extracting with benzol or acetone.
The latter extract was freed from solvent by evaporation, and the resulting resin treated as in (1).

In cases (1) and (4) the acid tar was distilled with steam and the residue was washed as free from acid as possible by diluting with three volumes of water, settling and decanting. Further attempts at washing resulted in persistent emulsification so that the tar was dried at 150° C.

On distilling the product at 300-350° C., a distillate smelling of crude creosote came over; this distillate was partially (15-20 per cent.) soluble in 10 per cent. caustic soda solution, so that the soluble part consisted of phenolic or cresolic bodies. The neutral portion yielded a reddish picrate from alcohol, melting at 105-115° C.

The residue dissolved partially in hot absolute alcohol and gave a deep blood-red picrate melting between 210° and 215° C. The original acid tar before distillation gave an intense bluish fluorescence when stirred with dilute caustic soda solution.

The residue decomposed at about 450-500° C. (estimated) into pitch and further smoky vapours smelling of crude creosote.

The upper fractions of kerosene gave these tests easily, but in the case of the 170-200° C. fraction very little result was obtained after distilling off the ordinary aromatics in steam.

Method (2) yielded red gelatinous deposits in each case, but in greater quantity with the higher fractions or complete kerosene.

These deposits were decomposed by water to an emulsion, which, on treatment with dilute acids, at once gave a reddish oily layer of specific gravity varying from 0·98 to 1·03 at 60° F. This liquid was acted on by concentrated sulphuric acid and, though quantities were too small to go through the whole procedure just described, indications showed that the same changes took place.

Method (3) with caustic soda gave, with the whole kerosene and with the 280-300° C. fraction, a deep red mass mixed with unchanged soda, which emulsified with water, and on neutralisation gave an impure yellow oil. (It was not possible to free this entirely from unchanged kerosene.) This oil was highly reactive and soon attained a very deep red colour, reacting with sulphuric acid to produce a tar.

The picrate formed from the oil was blood-red in colour, and melted at 79-82° C.

It is not difficult to follow these reactions on the assumption that indene, coumarone, fluorene and their homologues and oxidation products are present, whether produced pyrogenetically or otherwise.

Indene and its alkyl homologues, in addition to the properties given above, form para-indene resins with concentrated sulphuric acid or on standing; these form the basis, with coumarone products produced easily by their oxidation, of the indene and coumarone resin groups. The polymerised resins break up on distillation into phenolic bodies soluble in alkalies, alkyl benzenes, indene or coumarone and homologues which give picrates. Coumarone picrate melts at 102-3° C. The pitchy residues from the resins yield chrysene $C_{18}H_{12}$, picene $C_{22}H_{14}$, and pyrene $C_{16}H_{10}$. These bodies give fluorescent derivatives, sunlight bleaches their solutions, and pyrene gives a picrate, which, when pure, melts at 222°C. The hydrocarbons break up at 500°C.

Any indene or coumarone present in the 170-200° C. fraction is minute in quantity when the kerosene or crude is carefully distilled,

but cracking appears to favour their production and that of their homologues.

Indene and its homologues possess a reactive $-CH_2-$ group adjoining unsaturated atoms, and therefore have the property, in common with other bodies possessing this group, of forming sodium or potassium derivatives (–CHNa–) which are decomposed by water to re-form the oil and caustic soda.

The fraction 280-300° C., on treatment with solid caustic alkalies, gives red sodium or potassium derivatives of fluorene and its isomer γ-methylene diphenylene. These sodium salts break up with water or acids to fluorene which possesses a very reactive group, polymerising with loss of hydrogen to bi-fluorene and further to a deep red compound known as rubicene. The picrates of both fluorene and its isomer are blood-red and melt at 79-81° C., that of fluorene being stable in ether or toluene, that of the isomer in alcohol.

While cracked products have not been studied exhaustively here, it has been noticed that with local overheating of a kerosene under a reflux followed by rapid distillation, first runnings have been coloured yellow. After placing the distillate below 180° C. in the sun, it became darker and the portion not distilling below 150° C. oxidised quickly in the air, giving a product with about 30 per cent. of oxygen and of specific gravity 0·98 at 60° F. (analysis: C, 62·54 per cent.; H, 6·93 per cent.; O, 30·53 per cent.). This is not far from the analysis of $C_{10}H_{12}O_4$ (dicyclopentadiene diperoxide), but is by no means a pure compound, and the constitution is open to speculation. Another reaction which helps to isolate and identify the various unstable substances is their precipitation with anhydrous stannic chloride.[3] This reagent precipitates and resinifies them at once.

Further light is shed on the problem by the detailed examination of the upper end of the aromatics extracted by means of aniline.

Above 290° C. there is a marked difference in colour and reactivity. Though a cut from the crude was taken off with careful dephlegmation at 300° C., the aromatics gave a distillate up to 320° C. or higher.

Above 300° C., bromine values are of the order 10-12 per cent.; the substances are deep yellow on distillation but oxidise and turn dark visibly as one looks at them. On a further redistillation, the 300-320° C. fraction gave a dark residue, similar to an indene resin, and a yellow distillate which turned dark somewhat more slowly than before.

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[3] Torossian, *Jour. Ind. Eng. Chem.*, 1922, 13, 903.

It was difficult to make an accurate analysis on account of this rapid oxidation, but the following results were obtained:—

(1) Fraction 310-320° C. after darkening, gave sp. gr. at 60° F. 1·03, C 66·21 per cent., H 7·40 per cent., O 26·39 per cent. or $(C_3H_4O_{0\cdot9})_n$.

(2) Fraction 300-310° C., sp. gr. 1·026 gave a formula approximating to $(CHO_{0\cdot95})_n$.

This fraction gave benzoic acid on oxidation with chromic acid or permanganate; attempts to determine the molecular weight failed to give reliable results, which appeared to fluctuate widely around 230. It is probable that the fraction contains stilbene, $C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5$, b.pt. 306° C., also *pp*-dimethyl-stilbene, b.pt. 305° C. derived from the oxidation of toluene and *p*-xylene.

The oxidation of xylene to dimethyl stilbene by means of heating with sulphur to 300° C. is well known, but it has been found here that commercial xylene gives dimethyl stilbene on exposure in air to bright tropical sunlight, particularly in the presence of oxygen carriers.

The probability of the presence of xylene-styrene has already been mentioned, while another product traced is a di-polymer of indene boiling at about 310° C. with further resinification.

The immediate range above 295° C. may contain the following:—

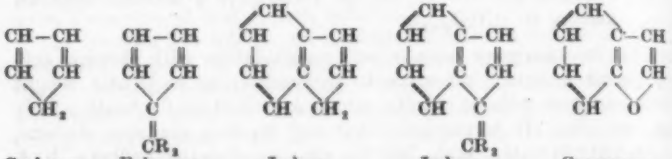
Xylene-styrene	B. pt. about 300° C.
Stilbene	306
pp-Dimethyl stilbene	305
Fluorene, γ-methylene diphenylene and allied bodies	295
Diphenylene oxide and dioxide	295—300
Phenyl-fluorene and its peroxide	Over 300
Xanthene $C_6H_4\langle{}^{O}_{CH_2}\rangle C_6H_4$	312
Naphthofurane	About 290
Dipolymers of indene, and indene-fulvenes ..	310—320

Indene-fulvenes or benzo-fulvenes (condensation products between the active —CH_2— group and the oxygen of aldehydes or ketones) are yellow bodies, and though their presence has not been definitely proved, they are suggested as condensation products produced in sunlight-reversion. It has been noticed that aromatics from reverting kerosenes turn deep orange-yellow very quickly in sunlight in the presence of benzaldehyde and ketones.

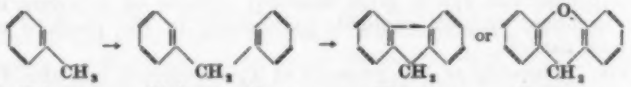
Besides the above, several condensation products with ordinary hydrocarbons are possible as well as some derivatives of the phenyl methanes. The effect of nitrogen and sulphur containing bodies has not been studied, but the total amount of sulphur in the crude itself does not exceed 0·2 per cent.

The fact observed in practice in the refinery as well as in the laboratory, that a kerosene with a final boiling point over 290° C. is very difficult to refine, and that this is a very definite limit, thus rests upon a clear foundation in theory.

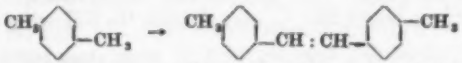
On glancing at the formulæ, it is possible to trace the relationships :—



Cyclopentadiene (Colourless unstable) | Fulvenes (coloured) | Indene (unstable) | Indene-fulvenes (coloured) | Coumarone.



Toluene Two mols. | Diphenylmethane | Fluorene | Xanthene



p-Xylene | *pp*-Dimethyl stilbene and oxidation products.

The catalytic action of substances which have already become acted upon by heat or in sunlight doubtless induces changes rapidly in those as yet untouched; for example, it has been mentioned that indene homologues condense with aldehydes and ketones with great ease to form deeply coloured indene-fulvenes, while fluorene, isolated through the sodium derivative, appears to do the same with more difficulty. Many of the fluorene derivatives change in sunlight, and absorb oxygen forming peroxides, but insufficient work has been done to discuss them in detail.

The work described obviously touches only on the fringe of the study of these unstable bodies, and while some of the experiments and deductions are conclusive, it is admitted that many gaps exist and that several deductions are controversial.

In pressure-cracked hydrocarbons, the presence of open chain unsaturateds of the isoprene type and olefines may have their effect, but it still remains probable that many of the effects of instability are produced by these five-ring compounds discussed above, and, indeed, ordinary olefines may well close up into ring formations

of this type; although the proportions present are far lower under ordinary conditions of distillation than in Coal-tar, yet good resins of the coumarone type, melting around 100° C., have been prepared from Burmah fractions and serve to confirm at least some of the deductions given.

Summary of Part I.

(1) The aromatics in fractions for Burmah crude up to 300° C. are present in maximum quantity over the range 140-190° C.; after a minimum at about 210° C., the content gradually rises until just above 290° C., when it increases suddenly. The average aromatic content under 125° C. is about 11-12 per cent. or 1·9 per cent. on the crude by volume and consists of benzene and toluene.

The content of aromatics in fractions of kerosene from 125° to 290° C. averages about 20 per cent. and is composed mainly of xylenes, cymene, pseudo-cumene and mesitylene below 180° C.

Above 180° and below 215° C., the predominant aromatics are the alkylated benzenes, which possess either small alkyl groups directly attached to the nucleus, or larger groups of the branching chain type rather than of normal chains. Above 215° C., the naphthalene alkyl derivatives are the chief constituents as shown by physical and chemical tests, but there still remains a proportion of the higher benzene homologues.

(2) Certain American sources give much the same qualitative results except that the tendency towards the branching chain compounds is not so evident.

Badarpur aromatics also show the same chief compounds, though the naphthalene and other polynuclear derivatives are in higher proportion and early fractions possess a relatively low aromatic content.

(3) The property of colour reversion is due to unstable resin-forming bodies, and some of these are members of the five-ring cyclopentadiene family, including indene, coumarone, fulvenes, fluorene and their homologues and condensation products.

There is a marked tendency towards the formation of peroxides of members of these classes, rather than of ordinary acid formation on oxidation.

(4) Colour reversion is present in all fractions of intentionally cracked hydrocarbons, but in straight carefully distilled

kerosenes begins at about the 180-190° C. fraction. Immediately above 290° C., the property of reversion is very marked in untreated distillates and is due mainly to the presence of a large number of unstable substances boiling around and about 300° C. and over, some of which have been identified as related to bodies mentioned in (3).

(5) Two types of colour reversion exist, *viz.*:—

(i) *In the dark.*—This is a polymerisation or condensation of existing products, not necessarily accompanied by further oxidation, and affects a small portion of the kerosene only. The effect is easily removed by refining methods. The coloured bodies produced can be "bleached" in sunlight, but are still unstable and then obey the sunlight reversion laws.

(ii) *In sunlight.*—This is due primarily to oxidation and subsequent polymerisation or condensation.
It is progressive and ultimately affects a large proportion of the oil. Only the most drastic removal of large quantities of hydrocarbons can prevent this change.

(6) The above properties are shared in common by petroleum fractions from several sources, *e.g.*, certain American kerosenes, Badarpur crude, Assam and East Indian crudes and others.

Part II.

The Aniline Critical Solution Temperature Test Applied to Kerosene Fractions.

The refining of East Indian and other kerosenes demands a ready means of testing for various classes of hydrocarbons, and, though practically no published work has appeared on the C.S.T. method as applied to fractions above 150° C., the test has been of great value locally for the last few years.

It has been subjected to many hundreds of cross checks during that time, and in spite of difficulties similar to those mentioned in two discussions[1, 2] on the unsaturateds in Petroleum spirits, it has been found to be a reliable and accurate method, in fact, more reliable and less tedious than determinations of loss in acid, or by nitration and other methods, although as yet the study has not been taken deeply into the examination of very highly unsaturated fractions.

Aniline, *o*-toluidine, furfural, glacial acetic acid, acetone and several other liquids all have their uses for C.S.T. work, and as

[1] *Journ. Inst. Petr. Techn.*, 1925, **11**, 537.
[2] *Ibid.*, 1926, **12**, 49.

reagents for refractionating out different classes of hydrocarbons; in conjunction with refractive index and specific gravity data on lines already suggested by Ormandy and Craven[3] they yield a great deal of useful information in the study of the composition of different crudes. The correlation of these different methods and their application to such problems will be deferred to a later paper, but the development of the C.S.T. test itself is now given.

It is true that aromatics in the range of naphthalene derivatives show less depression of aniline point for a given proportion of the aromatic than do the simpler members, but the difference is not great, and in a slumped kerosene boiling roughly between 125° and 300° C., the average standard curve will be correct to well under 1 per cent. on the kerosene. The accuracy will be even greater, if cracking is avoided, when suitable cuts are made and determined separately.

The general curve developed later in the paper is fairly accurate for ordinary white kerosenes of good market standard with a naphthene content of about 35-50 per cent. in its aromatic-free portion.

When the naphthene content is much higher, as in Badarpur fractions (which are practically pure naphthenes after aromatics are removed) or much lower as in a very paraffinoid kerosene, then it follows theoretically, and is confirmed practically (see Tables IX. and XXI.), that the depression of aniline point, produced by a known volume of aromatic, is slightly less or greater respectively than normal.

For example, taking hypothetical figures for clarity, suppose the An. Pt. of the aromatic were –20° C. and of the corresponding pure paraffin 80° C., so that each per cent. of aromatic depressed the aniline point about 1° C.

If enough naphthene were present to bring the An. Pt. of the aromatic free portion to 65° C., this would be 85° above the aromatic An. Pt. and each per cent. of aromatic would produce a depression of 0·85° C. instead of 1° C.

However, when aromatic content is reckoned by *weight* instead of by volume, the discrepancy disappears to a great extent owing to the fact that the specific gravities of the naphthenes are nearer than those of paraffins to those of the aromatics.

These points do not appear to have been given much attention in published work on the test for spirits.

Waterman and Perquin[4] observed that the effect on the aniline point of the addition of benzene, naphthalene and other aromatics

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[3] *Journ. Inst. Pet. Techn.*, 1924, **10**, 101.
[4] *Rev. trav. chim.*, 1922, **41**, 192. *J.S.C.I.*, 1922, **41**, 281A.

was not consistent with the amount of added hydrocarbon when the method was applied to unsaturated crudes. Although unsaturated and unstable bodies such as indene homologues, stilbene and oxidised products are present here (see Part I.), such considerations have not been proved to interfere seriously with the application of the method to Burmah, American, and even Badarpur crude fractions. The method has also been made to furnish information as to the chemical composition of lubricant fractions, though the quantitative data have not been worked out fully as yet.

The development of the Aniline C.S.T. method depends on the study of the following considerations:—

(1) The nature of the aromatics and kindred bodies.

(2) The effect of the purity of the aniline.

(3) The effects of different amounts and concentrations of sulphuric acid used in connection with the test on these fractions.

(4) Synthetic effects produced by the addition of known aromatics, naphthalene, naphthenes, terpenes and other bodies upon aniline points.

(5) The effects produced by the addition of aromatics actually isolated as a whole or in fractions by available methods, such as Armstrong's method or by means of aniline at suitable temperatures, from corresponding fractions of the crudes under examination.

Petroleum Spirits.

Tizard and Marshall's[6] work, with special reference to developments in the determination of naphthenes, as summarised later in Ormandy and Craven's paper,[7] was applied in conjunction with the actual isolation, by careful fractionation, of paraffins and naphthenes from early fractions of Burmah crude.

From this work, which constitutes a separate study to be discussed at another time, it appears that Ormandy and Craven's methods for the correlation of aniline points, gravities and refractive indices, can be applied with accuracy as long as some knowledge of the nature of the actual constituents can be obtained.

As applied generally to various sources, this correlation is apt to lose its accuracy owing to the rather wide variations in the specific gravities of individual paraffins and naphthenes of similar boiling point, but differing constitution. Refractive indices and

[6] *J.S.C.I.*, 1921, **40**, 20r.

aniline points give far more accurate general values than specific gravities for equi-boiling fractions.

Kerosene Fractions.

(1) *Nature of the Aromatics.*—This has already been dealt with at length in Part I. of this paper.

(2) *Purity of the Aniline.*—The effect of water on the C.S.T. of aniline or *o*-toluidine with hydrocarbons and fats is well known; applications of the principle appear in many papers, *e.g.*, Calcott, English and Dowling[6] estimate water in naphthalene by the C.S.T. in toluene, while Wood and Neale[7] estimate water in hydrocarbons by a similar method and Ormandy and Craven[8] have found it necessary to correct certain figures altered by the presence of moisture.

The writer has found that the addition of water to a homogeneous aniline-hydrocarbon mixture about 5° C. above the C.S.T. provides a useful auxiliary means of fractionating classes of hydrocarbons by separation.

The following results show the difference in the case of a kerosene before and after treatment with three volumes of 98 per cent. H_2SO_4, aniline from the same bottle being taken in each case:—

	Arom. free kerosene. Sp. gr. 0·7890 at 60° F. ° C.		Original kerosene. Sp. gr. 0·832 at 60° F. ° C.
Aniline point with dry aniline ..	71·8	..	60·4
Aniline point with wet aniline (shaken with water at 30° C. and separated)	97·4	..	85·0

The differences remain nearly, though not quite the same, but the C.S.T.'s are by no means as sharply defined with wet as with dry aniline.

The C.S.T. curves for different hydrocarbons, obtained with aniline containing varying degrees of moisture, are nearly parallel and, unless absolute values are required, the error in aromatic estimation produced by taking differences in aniline points before and after acid treatment will not be large with any except saturated aniline.

In all cases, however, it is advisable to use freshly distilled aniline dried with anhydrous potassium carbonate; the hydrocarbons under test should be dried with calcium chloride after being well washed with water in the case of acid-treated oils.

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[6] *J. Ind. Eng. Chem.*, 1924, **16**, 27.
[7] *Journ. Inst. Petr. Techn.*, 1925, **11**, 471.
[8] *Ibid.*, 1926, **12**, 89.

In the present work, the actual tests have been applied in accordance with the usual procedure for spirits, using equal volumes of aniline and oil.

o-Toluidine gives practically identical results throughout except for the fact that the C.S.T. is 46° C. below that given by aniline for the same oil.

Neither reagent after use in the test can be used again before chemical purification by means of solution in dilute acid, liberation by alkali, extraction with ether, distillation and drying.

(3) *Effects of Amount and Concentration of Sulphuric Acid.*—Papers by Houghton and Bowman[9], Moore and Hobson[10] and Ormandy and Craven[11] deal with the effect of different concentrations and amounts of sulphuric acid on the removal of unsaturateds and aromatics; the subject has also received attention and discussion in the symposium on unsaturated hydrocarbons[3].

The results obtained below indicate that nearly all ordinary aromatics (even when known aromatics are used with aromatic-free hydrocarbons) are certainly acted upon by 85 per cent. acid and higher concentrations, and the series obtained suggest some modification in the views expressed in the references given. For this reason, details of a number of trials are appended in full.

TABLE I.

Untreated kerosene of range 150—300° *C. Aromatic content approx.* 20% *by weight.*

(*a*) Three volumes acid agitated with oil for half an hour—

Concn. acid.	Original kero.	75%	80%	85%	90%	95%	98%
Loss in acid treatment by vol.	—	nil	nil	2%	7%	12%	20%
Sp. gravity 60° F. ..	0·813	0·8136	0·8135	0·8130	0·8035	0·7945	0·7895
Aniline point, ° C. ..	53·8	54·0	54·0	54·5	62·5	68·0	71·4
Iodine value, % ..	0·9	—	0·34	0·27	0·17	0·10	nil
(*b*) Three volumes acid for three hours—							
Loss in acid	—	2%	2%	3%	8%	13%	20%
Sp. gr., 60° F. ..	0·813	0·8106	0·8095	0·8115	0·7976	0·7896	0·7880
Aniline point, ° C. ..	53·8	54·0	54·0	54·7	64·8	69·6	71·4
(*c*) One volume acid for half an hour—							
Loss	—	nil	2%	2½%	7%	10%	18%
Sp. gr., 60° F. ..	0·813	0·813	0·8144	0·8134	0·8094	0·7995	0·7904
Aniline point, ° C. ..	53·8	53·8	53·8	54·0	58·0	65·6	70·4

The same kerosene was fractionated, yielding on distillation: Under 200° C., 58 per cent.; 200—250° C., 32 per cent.; over 250° C., 10 per cent.

[9] *Journ. Inst. Petr. Techn.*, 1925, **11**, 583.
[10] *Ibid.*, 1925, **11**, 587.
[11] *Ibid.*, 1926, **12**, 68.

TABLE II.

The fraction under 200° C.

(*a*) Three volumes acid for half an hour—

	Orig.	75%	80%	85%	90%	95%	98%
Sp. gr., 60° F. ..	0·801	0·791	0·791	0·7894	0·7794	0·7728	0·771
Aniline point, ° C. ..	46·6	47·0	47·0	47·4	57·0	63·0	64·5

(*b*) Three volumes acid for three hours—

Sp. gr., 60° F. ..	0·801	0·790	0·7895	0·784	0·7765	0·770	0·769
Aniline point, ° C. ..	46·6	47·2	47·6	48·2	58·0	63·4	64·5

(*c*) One volume acid for half an hour—

Sp. gr., 60° F. ..	0·801	0·793	0·793	0·7885	0·784	0·778	0·774
Aniline point, ° C. ..	46·6	47·0	47·0	47·2	56·2	62·4	64·4

TABLE III.

Fraction 200—250° C.

(*a*) Three volumes acid for half an hour—

Concentration.	Orig.	75%	80%	85%	90%	95%	98%
Sp. gr., 60° F. ..	0·8270	0·8270	0·8268	0·8258	0·8153	0·8088	0·8018
Aniline point, ° C. ..	59·4	59·4	59·4	59·6	65·6	70·0	75·8

(*b*) Three volumes acid for three hours—

Sp. gr., 60° F. ..	0·8270	0·8270	0·8255	0·8242	0·8125	0·8064	0·8000
Aniline point, ° C. ..	59·4	59·4	59·4	59·8	66·6	72·2	75·8

(*c*) One volume acid for half-an-hour—

Sp. gr., 60° F. ..	0·8270	0·8270	0·8270	0·8258	0·8165	0·8100	0·8020
Aniline point, ° C. ..	59·4	59·4	59·4	59·5	64·8	69·6	75·8

From the above three tables it is seen that—

(1) Three volumes of acid give the better effect.

(2) Agitation for three hours gives appreciably more removal with intermediate concentrations of acid, but 98 per cent. acid can act efficiently in half an hour.

(3) In a few cases there is an increase of gravity with 75 per cent. and 80 per cent. acids. This is more noticeable below. Note also Ormandy and Craven's results with spirits[13] and the terpene series in Tables XII. and XIII. below.

(4) It is impossible to rely on specific gravity effects, in fact, Thole's method is in any case inapplicable with accuracy unless the actual aromatic specific gravities are known. Losses of hydrocarbon on acid treatment are also not reliable when done on a small scale, and bear no comparison with the accuracy of the aniline point determinations.

(5) The aniline point rises steadily in spite of changes in gravity. See Fig. 1.

[13] *Journ. Inst. Petr. Techn.*, 1926, **12**, 68.

(6) The effect of unsaturation on the aniline points is not marked. The iodine values of a series of treatments with the same kerosene is shown in Table I.

(7) There is a great increase in the action of the acid on the aromatics between concentrations of 85 per cent. and 90 per cent.

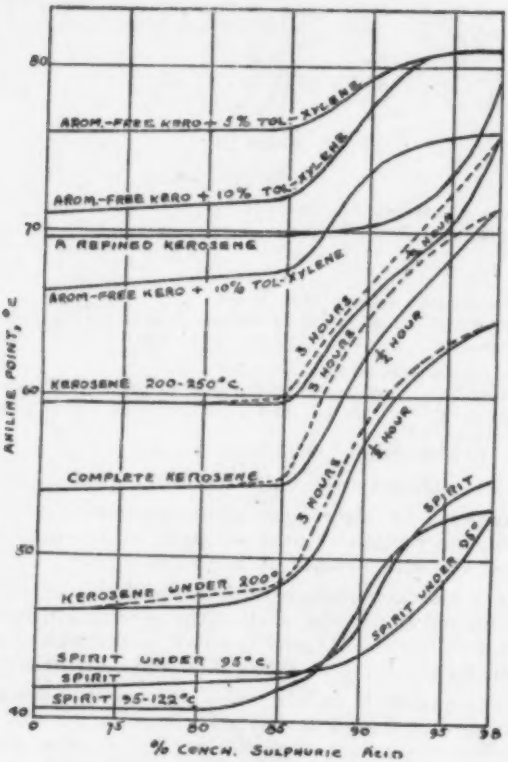


FIGURE 1.

The action of 87½ per cent. acid is given in the curves in Fig. 1.

The action on aromatics was examined further by using pure aromatics extracted from kerosene, also mixtures of toluene and xylene, 1:3 by volume.

TABLE IV.

Aromatics agitated with three vols. sulphuric acid for half an hour. Acid concentrations and solubility.

Aromatic	80% acid	90%	98%
Benzene	Low ..	5% ..	100%
Toluene-xylene (1 : 3) ..	7·5% ..	32·5% ..	100%
Aromatics from kerosene under 210° C.	5% ..	20—25% ..	100%
Aromatics, 210—270° C. ..	10% ..	30% ..	100%

In the next series, toluene-xylene mixture was added in known proportions to aromatic-free kerosenes of range 150-300° C.

TABLE V.

Aromatic-free kerosenes + T.X. mixture. Acid treatment—three vols. for half an hour.

(*a*) Burmah aromatic-free 95%, T.X. mixture 5% by volume—

Concn. acid.	Orig. kero.	75%	80%	85%	90%	92·5%	95%	98%
Sp. gr., 60° F.	0·7925	0·7965	0·7960	0·7955	0·7935	0·7925	0·791	0·7905
Aniline pt. °C.	71·0	71·0	71·0	71·2	74·6	75·2	75·4	75·6

(*b*) American aromatic-free 95%, T.X. mixture 5% by volume—

Sp. gr., 60° F.	0·7996	0·8012	0·8010	0·8002	0·7992	0·7982	0·7972	0·7970
Aniline pt. °C.	76·0	76·0	76·0	76·2	79·4	80·3	81·0	81·0

(*c*) Burmah aromatic-free 90%, T.X. mixture 10% by volume—

Sp. gr., 60° F.	0·7990	0·7992	0·7982	0·7980	0·7937	0·7932	0·7903	0·7902
Aniline pt. °C.	66·4	66·4	67·0	67·6	73·8	75·4	75·6	75·6

(*d*) American aromatic-free 90%, T.X. mixture 10% by volume—

Sp. gr., 60° F.	0·8026	0·8050	0·8052	0·8037	0·7992	0·7982	0·7974	0·7972
Aniline pt. °C.	71·2	71·2	71·4	72·0	77·6	80·2	81·0	81·0

TABLE VI.

A refined American kerosene from the market.

(*a*) Agitation with three vols. acid for half an hour—

Concn. of acid.	Orig. kero.	75%	80%	85%	90%	95%	98%
Sp. gr., 60° F.	0·8095	0·8095	0·8094	0·8105	0·8085	0·804	0·795
Aniline pt. °C.	69·6	69·6	69·8	69·8	71·4	73·4	79·0

(*b*) Agitation with three volumes acid for three hours—

Sp. gr., 60° F.	0·8095	0·8095	0·8090	0·810	0·8075	0·803	0·794
Aniline pt. °C.	69·6	69·6	69·6	69·8	71·6	74·0	79·0

The above kerosene had an iodine value of 2·3 per cent. with 10–11 per cent. aromatics, but the unsaturation did not appear to affect the aniline points.

TABLE VII.

Burmah heavy motor spirit.

(21% under 100° C., F.B.P. 160° C. by A.S.T.M. distillation.)

(*a*) Three volumes acid for half an hour—

Concn. of acid.	Orig. kero.	75%	80%	85%	90%	95%	98%
Sp. gr., 60° F.	0·7597	0·763	0·763	0·7625	0·7565	0·748	0·747
Aniline pt. °C.	42·0	42·0	42·4	42·6	45·8	53·4	54·8

(*b*) Three volumes acid for three hours—

Sp. gr., 60° F.	0·7597	0·761	0·7615	0·7605	0·753	0·7465	0·746
Aniline pt. °C.	42·0	42·0	42·4	42·6	49·2	54·6	55·0

(*c*) One volume acid for half an hour—

Sp. gr., 60° F.	0·7597	0·7615	0·761	0·761	0·760	0·751	0·747
Aniline pt °C.	42·0	42·0	42·2	42·4	44·0	50·6	54·8

TABLE VIII.

The same Burmah spirit fractionated: (1) Below 95° C., 20% by vol.; (2) 95—122° C., 62%; (3) over 122° C., 18%.

(1) *Fraction under* 95° C.

(*a*) Three volumes acid for half an hour—

Concn. acid.	Orig. kero.	75%	80%	85%	90%	95%	98%
Sp. gr., 60° F.	0·733	0·7355	0·736	0·737	0·734	0·730	0·722
Aniline pt. °C.	43·0	43·0	43·0	43·0	44·0	48·4	52·6

(*b*) Three volumes acid for three hours—

Sp. gr., 60° F.	0·733	0·734	0·734	0·7335	0·7325	0·7295	0·721
Aniline pt. °C.	43·0	43·0	43·0	43·0	44·0	48·6	53·0

(*c*) One volume acid for half an hour—

Sp. gr., 60° F.	0·733	0·734	0·7375	0·737	0·736	0·7335	0·725
Aniline pt. °C.	43·0	43·0	43·0	43·0	43·2	47·3	52·6

(2) *Fraction* 95—122° C.

(*a*) Three volumes acid for half an hour—

Sp. gr., 60° F.	0·7595	0·761	0·760	0·7595	0·753	0·747	0·745
Aniline pt. °C.	40·6	40·6	40·6	41·8	46·8	52·4	53·0

(*b*) One volume acid for half an hour—

Sp. gr., 60° F.	0·7595	0·762	0·761	0·7595	0·756	0·749	0·745
Aniline pt. °C.	40·6	40·6	40·6	41·0	44·8	52·2	53·0

(3) *Fraction over* 122° C.

(*a*) Three volumes acid for half an hour—

Sp. gr., 60° F.	0·772	0·774	0·774	0·7725	0·762	0·757	0·7565
Aniline pt. °C.	43·2	43·2	43·6	44·0	54·2	57·6	58·6

(*b*) Three volumes acid for three hours—

Sp. gr., 60° F.	0·772	0·772	0·7715	0·771	0·758	0·754	0·754
Aniline pt. °C.	43·2	43·4	43·8	44·8	55·2	58·4	58·6

(*c*) One volume acid for half an hour—

Sp. gr., 60° F.	0·772	0·7735	0·7735	0·773	0·765	0·758	0·7565
Aniline pt. °C.	43·2	43·2	43·4	43·6	54·0	57·4	58·6

The differences in behaviour of benzene, toluene and xylene are shown clearly in the last series; benzene requires strong acid, while toluene and xylene are more easily sulphonated by less concentrated acid, according to the time of agitation.

It will be inviting considerable inaccuracy in the determination of aromatics to use acid much over 80 per cent. in strength, and even 85 per cent. has an appreciable effect on this class of hydrocarbons.

(4) The Effect of the Addition of Known Compounds or Classes of Hydrocarbons on Aniline Points.

(a) *Aromatics.*

Table IX.

Addition of known aromatics to aromatic-free kerosenes.

Aromatic used: Toluene-xylene mixture 1 : 3 by volume. In each case n% is added to 100-n% of aromatic-free kerosene. Aromatic-free kero. Burmah, American (Elephant brand) and Badarpur 150—300° C. fractions treated three times at six hours with three volumes 98% H_2SO_4.

Aromatics, % by vol.	Burmah. An. pt. % by weight.	Burmah. 69·6° C. An. pt. depression.	American. An. pt. % by weight.	American. 71·0°C. An. pt. depression.	Badarpur. An. pt. % by weight.	Badarpur. 59·6° C. An. pt. depression.
5	5·4	4·5	5·4	4·6	5·1	4·2
10	10·8	8·8	10·7	9·0	10·1	8·4
15	16·2	13·6	16·0	13·6	15·2	12·6
20	21·5	18·4	21·3	18·4	—	—
25	26·7	23·2	26·5	23·2	—	—
30	31·9	28·2	31·7	28·6	—	—
35	37·1	33·4	36·8	33·4	—	—
40	42·2	39·0	41·9	39·0	—	—

Results intermediate to those above were obtained by adding Badarpur aromatic-free kerosene in varying proportions to Burmah or American aromatic-free bases.

The lower the aniline point of the aromatic-free portion, the smaller, in some degree, is the depression of the aniline point produced by a given amount by *volume* of aromatic as mentioned previously; when aromatic content is taken by weight, most of the discrepancy disappears.

Taking 70° C. as a good average figure for the aniline point of a normal aromatic-free kerosene of good burning properties and containing some 40 to 50 per cent. of naphthenes, the above, with several scores of determinations not included here, show that on the volume basis a correction a little less than the percentage represented by the difference between the aniline point of the aromatic-free portion and 70° C. should be added to, or subtracted from, the actual depressions obtained before the standard curve is used. Otherwise, it will be better to make a standard curve for the particular crude under investigation.

If fractions are being dealt with instead of kerosene as a whole, the curves developed in Fig. 2 will show average aniline point, for different naphthene contents of given boiling ranges and may be used in a similar manner.

These points are more of theoretical than practical interest, for if the naphthene content is abnormally high, the kerosene will not burn well except in special fuel burners, while there are few ordinary kerosenes with much lower naphthene and higher paraffin

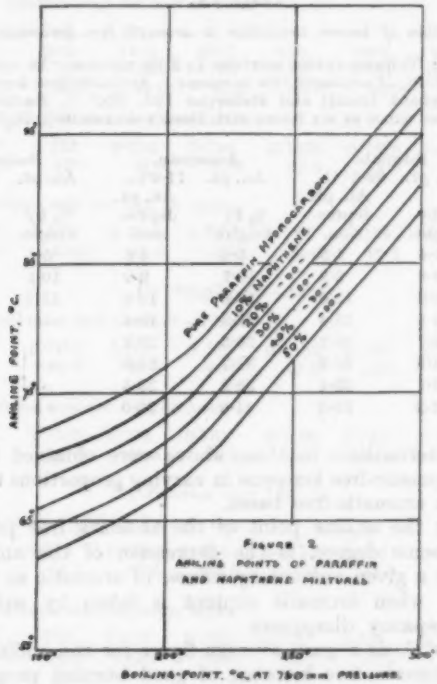


FIGURE 2.
ANILINE POINTS OF PARAFFIN AND NAPHTHENE MIXTURES.

contents, except in certain special cases where low-melting paraffins are employed as solid illuminants. In this case, the correction is naturally applied the other way.

(b) *Naphthalene.*

TABLE X.

Solutions of naphthalene in aromatic-free high kerosene cuts, made up by weight.

Mixture.	An. pt. untreated. °C.	An. pt. 98% acid treated. °C.	Depression. °C.
100% A.F. kero.	75·0 ..	75·0 ..	—
97½% K.+2½% N.	72·9 ..	75·0 ..	2·1
95% K.+5% N.	70·9 ..	75·0 ..	4·1
90% K.+10% N.	66·7 ..	75·0 ..	8·3

Similar mixtures with ordinary kerosene :—

Mixture.	An. pt. untreated. ° C.	An. pt. 98% acid treated. ° C.	Depression. ° C.	*Correction to add. ° C.	Corrected depression due to naphthalene. ° C.
100% kero	60·0	77·3	17·3	0	0
97½% K.+ 2½% N. ..	58·4	77·3	18·9	0·4	2·0
95% K.+5% N. ..	56·8	77·3	20·5	0·9	4·1
90% K.+10% N. ..	53·4	77·3	23·9	1·7	8·3

* NOTE.—To get the true effect of naphthalene it has to be remembered that sufficient aromatics are originally present to depress the A. pt. by 17·3° ; in the last case, 100 pts. of mixture contain only nine-tenths of these, hence 17·3° less 1·7° is the effect due to these and the remainder to the naphthalene.

The depressions for naphthalene obtained above are somewhat less than for T.X. mixture, but agree well with those obtained for aromatics extracted from kerosene fractions of the suitable range (see later).

Other pure aromatics were only available from kerosene sources.

(c) *Naphthenes.*—The only pure naphthenes available were hexahydrobenzene, and medium Badarpur aromatic-freed fractions, which by gravity, refractive index and apparently aniline point values, appeared to be practically pure naphthenes with a highly terpenic smell.

Trials with varying proportions of hexahydrobenzene (sp. gr. 0·7805 at 60° F., an. pt. 32° C.) added to various aromatic-free fractions of Burmah and American kerosenes boiling at 150° C., 200° C., 250° C. gave a depression of 4° C. per 10 per cent. content, when corrected in a manner similar to that applied to naphthalene above, based on the known aniline points of pure paraffins of the same b.pt. range (see Fig. 2). This is the same figure as that given in published work[3] for naphthenes in the spirit fraction below 95° C.

TABLE XI.

Addition of Badarpur naphthenes to Burmah and American aromatic-free kerosenes containing 50% and 40% naphthenes already.

Mixture.	Depression An. pt.	Mixture.	Depression An. pt.
50% paraffin+50% naphthene (original) ..	—	60% P.+40 N. (orig.) ..	—
45% P.+55% N. .. (*i.e.*, 90% original+10% Badarpur naphthene)	1·0	54% P.+46% N. .. (90% orig.+10% Bad. naphthene)	1·2
40% P.+60% N. ..	2·2	48% P.+52% N. ..	2·5
35% P.+65% N. ..	3·8	(80% orig.+20% Bad. N.)	

The above cannot be taken as more than an indication, as the assumption is made that the existing and added naphthenes have similar effects. Other methods of estimation (*e.g.*, by gradual destruction of naphthenes by fuming HNO_3, specific gravity and optical considerations) confirm that a difference of 5 per cent. in naphthene content gives a depression of 1° C. in aniline point approximately, and that in this range, the aniline points of the naphthenes lie about 20° C. below those of the paraffins with similar numbers of carbon atoms, though in the spirit fractions the difference is greater.

(d) *Terpenes.*—Distillation cuts at 150-160° C. and 160-170° C. were taken from pure American turpentine to represent pure terpenes corresponding to the formula $C_{10}H_{16}$. Mixtures of these were made up with aromatic-free and ordinary kerosene fractions; the aniline points were then taken after agitation with acid of various concentrations.

Specific gravities are given as they illustrate the same changes as those shown in Tables I.—VIII.

TABLE XII.

Terpene.—150—160° C. cut from turpentine.
Aromatic-free kerosene, sp. gr. 0·799 at 60° F.; an. pt., 78·6° C.
Acid.—Three volumes of concentration given.
Mixtures.—97½% A.F.K.+2½% terp.; 95% A.F.K.+5% terp.

Concn. acid. %	2½% Mixture. Sp. gr. 60° F.	2½% Mixture. An. pt. ° C.	5% Mixture. Sp. gr. 60° F.	5% Mixture. An. pt. ° C.
nil	0·8002	77·0	0·8023	76·0
70	0·8045	77·4	0·8065	76·6
75	0·8032	77·8	0·8045	77·2
80	0·8022	78·0	0·8036	77·4
85	0·8015	78·4	0·8028	78·0
98	0·8002	78·6	0·8008	78·6

TABLE XIII.

Aromatic-free kerosene, sp. gr. 0·7986; an. pt., 77·4° C. with 160—170° C. terpenes.

Conc. of acid, %	2½% Mixture. Sp. gr.	2½% Mixture. An. pt. ° C.	5% Mixture. Sp. gr.	5% Mixture. An. pt. ° C.	10% Mixture. Sp. gr.	10% Mixture. An. pt. ° C.
nil	0·7985	75·6	0·801	74·4	0·805	71·8
70	0·8016	76·0	0·8046	74·8	0·8095	73·2
75	0·8016	76·2	0·8031	75·4	0·808	74·2
80	0·8016	76·2	0·8026	75·8	0·8065	74·6
85	0·801	76·4	0·8026	76·0	0·8055	75·2
98	0·797	77·4	0·7986	77·4	0·7980	77·4

TABLE XIV.

Ordinary kerosene with terpenes.

Conc. acid. %	Original kero. An. pt., °C.	2½% Mixture. An. pt., °C.	5% Mixture. An. pt., °C.	10% Mixture. An. pt., °C.
(*a*) With 150—160° C. terpenes—				
nil	54·4	53·5	52·6	51·2
70	54·4	53·6	53·8	52·0
80	54·8	54·1	54·6	53·8
85	54·8	54·8	56·4	55·0
98	71·2	71·2	71·2	71·2
(*b*) With 160—170° C. terpenes—				
nil	54·4	53·2	52·4	50·6
80	54·6	54·4	54·0	53·4
98	71·2	71·2	71·2	71·2

Corrected depressions of aniline point for nil acid treatment owing to decrease in original aromatics brought about by lowering the percentage as more terpenes are added (as in the naphthalene series) are as follows :—

(a) 2½%. 1·3; 5%, 2·6; 10%, 4·9.

(b) 2½%, 1·2; 5%, 2·8; 10%, 5·5.

Conclusions.—Depressions in aniline point average 0·5° per 1 per cent. terpene.

Differences between aniline points of untreated and 80 per cent. acid-treated mixtures are 0·3° per 1 per cent. terpene.

Most of the terpene is removed by 85 per cent. acid.

The properties of the terpene fractions themselves are :—

150-160° C. Sp. gr. 0·8705 Aniline pt. 15·0° C.
160-170° C. Sp. gr. 0·8765 Aniline pt. 8·6° C.

Both are completely soluble in 98 per cent. H_2SO_4.

THE ANILINE POINTS OF DIFFERENT KEROSENE FRACTIONS.

Knowing the effect of certain known substances on the aniline point, it remains to be seen how aniline points vary with rising fractions.

As to acid, the use of 98 per cent. and 80 per cent. or 98 per cent. and nil concentrations will give the data necessary. Terpenes are not present in appreciable quantities in the kerosenes under examination and, in any case, from the marketing point of view, they may be regarded as producing effects similar to those produced by true aromatics giving equal depressions of aniline point. It is not safe to use 85 per cent. acid in estimating aromatics, as some of the latter are acted upon, so that in the following series the differences of aniline point between 98 per cent. acid-treated

(with three volumes of acid agitated for half an hour) and non-acid-treated fractions are taken.

Aniline points rise with the boiling point of the fraction as seen in the following cases obtained with crudes or kerosenes from the sources named. These values are extracted from more complete tables which indicate the composition of the oils in question and which will be discussed at some other time :—

TABLE XV.

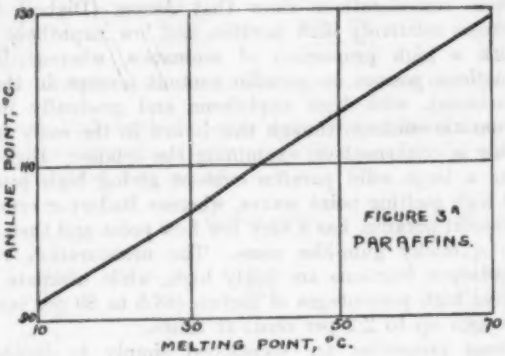
Fraction temp., °C.	Description of source of fraction.	Sp. gr. 60° F. arom.-free portion.	An. pt. arom.-free portion.	Difference an. pt. before & after acid treatment.	Diff. sp. gr. before & after acid.
125—130	Burmah crude	0·7536	59·8	16·0	0·0188
	An American kerosene (refined) ..	0·7610	55·0	4·6	0·0065
	Punjab crude	0·7459	59·0	20·8	0·0249
145—150	Burmah crude	0·7610	63·4	19·3	0·0228
	American refined ..	0·7765	57·2	5·4	0·0069
	Punjab crude	0·7583	62·1	24·9	0·0284
	Badarpur crude ..	0·7880	55·8	11·8	0·0109
	Assam (Digboi) crude ..	0·7510	65·0	28·6	0·0324
195—200	Burmah crude	0·7876	72·1	15·5	0·0216
	American refined ..	0·8043	64·8	9·6	0·0109
	Punjab crude	0·7936	68·6	17·8	0·0178
	Badarpur crude ..	0·8398	58·5	24·2	0·0196
	Assam crude	0·7812	72·6	23·8	0·0274
245—250	Burmah crude	0·8072	78·9	17·7	0·0324
	American refined ..	0·8190	77·4	9·8	0·0141
	Punjab crude	0·8109	77·5	16·0	0·0236
	Badarpur crude ..	0·8730	64·4	37·2	0·0388
	Assam crude	0·8018	82·4	22·0	0·0380
270—275	Burmah crude	0·8156	86·2	21·9	0·0390
	American refined ..	0·8244	81·6	10·6	0·0169
	Punjab crude	0·8286	82·5	17·5	0·0270
	Badarpur crude ..	0·8894	67·4	47·5	0·0448
	Assam crude	0·8104	87·2	24·4	0·0446

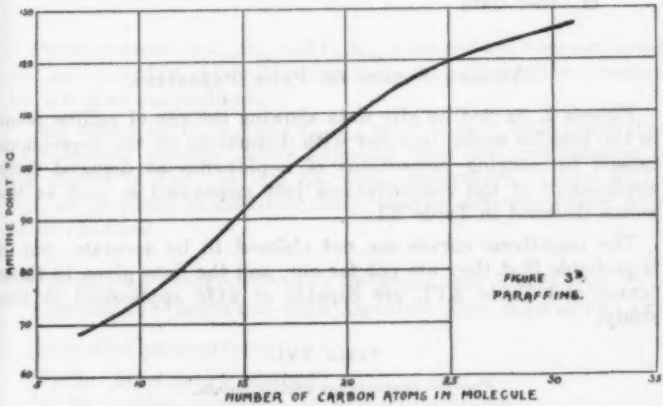
A few points bearing on the relative composition of the above may be noted, *viz.* :—

(1) The higher the specific gravities of aromatic-free fractions of similar boiling point range, the lower are the aniline points.

(2) The differences in specific gravity before and after acid treatment are misleading if compared as absolute values; *e.g.*, Badarpur and Assam (Digboi) 270-275° C. fractions show similar gravity differences, but differ widely in aromatic content.

This is natural considering that the Badarpur naphthene portion has a gravity more nearly equal to that of the extracted aromatics.





The point illustrates the impossibility of applying to these fractions a gravity method similar to that of Thole for spirits.

(3) On applying Ormandy and Craven's[3] method of correlating specific gravities and refractive indices with absolute aniline points for aromatic-free spirits as a rough method for the

estimation of naphthenes, the fractions in Table XV. yield information as to the approximate composition, although specific gravities alone cannot be made an accurate basis for estimation.

(4) These considerations show that Assam (Digboi) fractions possess relatively high paraffin and low naphthene content with a high proportion of aromatics, whereas Badarpur fractions possess no paraffin content (except in the lowest fractions), with high naphthene and gradually increasing aromatic content, though this is low in the early fractions. This is confirmed on examining the crudes; Digboi crude has a large solid paraffin content giving high proportions of high melting point waxes, whereas Badarpur crude yields no solid paraffin, has a very low flow point and then congeals to a sticky gum-like mass. The unsaturation values of Badarpur fractions are fairly high, while ultimate analysis gives high percentages of carbon (88·5 to 89 per cent.) with oxygen up to 2·2 per cent. at times.
These properties are mentioned simply to indicate how observations on the aniline point can assist the confirmation of other data.

Aniline Points of Pure Paraffins.

Figures 2, 3A and 3B give data showing the rise of aniline point in the paraffin series, together with deductions on the depressions caused by varying proportions of naphthenes as deduced from applications of the considerations just mentioned as well as the points deduced in Table XI.

The naphthene curves are not claimed to be accurate, but it is probable that they are not far out, and the data given in these curves and Table XVI. are capable of wide application in this study.

Table XVI.

Paraffin hydrocarbon aniline points.

(See Figs, 2, 3A, 3B.)

Hydrocarbon.	Boiling pt.	Aniline pt.
C_7H_{16} (normal) ..	98·4° C. ..	68° C.
C_9H_{20}	149·5° C. ..	72—74° C.

The four following hydrocarbons were obtained from narrow fractions of Burmah crude freed from naphthenes and aromatics by means of fuming nitric and sulphuric acids, separation and

redistillation. They represent mixtures of isomers of the formula given, boiling within the temperature range shown:—

Hydrocarbon.	B. pt. °C.	B. pt. fraction.	Aniline pt. °C.
$C_{11}H_{24}$ ..	194·5* ..	195—200 ..	77—78
$C_{14}H_{30}$ ..	252·5* ..	250—255 ..	88
$C_{16}H_{34}$ ..	270·5* ..	270—273 ..	92—93
$C_{17}H_{36}$ ..	303·0* ..	300—305 ..	99

*Note.—Values for the normal hydrocarbons at 760 mm. pressure.

The seven hydrocarbons below were recrystallised from Burmah wax with the exception of the one melting at 56° C., which came from an American wax sample:—

Hydrocarbons.	Melting point. °C.	Aniline point. °C.
$C_{21}H_{44}$ ..	40·4 ..	111
$C_{23}H_{48}$ ..	44·4 ..	113·5
$C_{24}H_{50}$ ..	52·0 ..	117·5
Approx. $C_{25}H_{52}$ ..	56 ..	120·0
,, $C_{26}H_{54}$ ..	61 ..	123
,, $C_{28}H_{58}$ .. } or $C_{29}H_{60}$ .. }	67 ..	127
$C_{37}H_{116}$ ..	95 ..	154

(Refined Fields wax.)

Paraffins between $C_{17}H_{36}$ and $C_{21}H_{44}$ have not yet been extracted, but are probably obtainable from early wax-oil distillate fractions by refrigeration methods.

The values for $C_{11}H_{24}$ and $C_{14}H_{30}$ seem to be a little lower than pure normal paraffin values expected from the interpolation of the curves in Figs. 3A and 3B, which suggest 80° C. and 90° C., but, as prepared at different times, slightly different values have been obtained.

(5) Effect on Aniline Points of Aromatics Extracted from Kerosenes: Mixtures with Aromatic-Free Kerosene Cuts.

Aromatics were extracted:—

(1) By Armstrong's method.
(2) By aniline extraction at low temperatures.

The sources were Burmah and Badarpur crude fractions, also an American kerosene from the market.

The aromatics obtained by Armstrong's method were 100 per cent. pure; those obtained by aniline extraction methods were not quite pure, but they were used as they stood after re-extraction, and the proportion of aromatics in them was determined by

independent means. The general nature of these aromatics will be seen on reference to Part I.
The methods adopted were:—

(1) Fractions of the kerosene were extracted separately and the corresponding aromatic cuts were kept by themselves.

(2) The kerosene was extracted as a whole and the aromatics used either as a whole, or fractionated subsequently for use with corresponding aromatic-free portions.

The aromatic-free portions were in all cases obtained by three treatments, each with three volumes of 98 per cent. sulphuric acid on a water bath for some hours with occasional agitation.

TABLE XVII.

Data for fractions employed in Tables XVIII. to XX. inclusive.

Fraction, °C.	Sp. gr. 60° F. Arom.-free portion.	Sp. gr. Aromatics.	Aniline pt. Arom.-free portion.	Iodine value. Aromatics.
125—150	0·760	0·866	60·6	1·8
150—180	0·773	0·872	67·2	1·9
180—200	0·785	0·882	69·0	2·7
125—215	0·780	—	67·4	—
215—230	0·797	0·910	75·3	3·4
230—250	0·805	0·930	79·2	5·2
250—270	0·812	0·945	82·4	5·5
Over 270	—	1·03	—	17·6
Complete kerosene	0·790	0·896	71·2	—

TABLE XVIII.

Addition of different aromatic fractions to the same aromatic-free kerosene, 125—215° C. fraction.

% Aromatics by vol. for all columns.	Aromatic fraction, 125—150° C.		Aromatic fraction, 150—180° C.		Aromatic fraction, 180—200° C.	
	% Arom. by weight.	An. pt. depression. ° C.	% Arom. by weight.	An. pt. depression. ° C.	% Arom. by weight.	An. pt. depression. ° C.
1	1·12	1·0	1·12	1·0	1·13	0·9
2	2·2	1·8	2·2	1·8	2·3	1·6
3	3·3	2·8	3·3	2·8	3·4	2·5
5	5·5	4·6	5·6	4·4	5·6	4·2
8	8·8	7·5	8·9	7·3	9·0	6·7
10	11·0	9·2	11·1	9·2	11·2	8·4
12	13·2	11·0	13·2	10·7	13·4	10·0
14	15·3	13·0	15·4	12·7	15·5	11·9
15	16·4	14·1	16·5	13·6	16·6	12·6
16	17·5	15·0	17·6	14·4	17·7	13·4
18	19·6	17·0	19·7	16·2	19·9	15·2
20	21·7	18·6	21·8	18·4	22·1	16·8
22	23·8	20·8	24·0	20·0	24·2	18·8
25	27·0	23·8	27·1	23·3	27·4	21·5
30	32·2	29·0	32·4	27·6	32·6	26·0

TABLE XIX.

Addition of different aromatic fractions to their corresponding aromatic-free cuts. (See Fig. 4.)

% Aromatics by vol. for all columns.	Fraction 125—150° C.		Fraction 150—180° C.		Fraction 180—200° C.	
	% Arom. by weight.	An. pt. depression. ° C.	% Arom. by weight.	An. pt. depression. ° C.	% Arom. by weight.	An. pt. depression. ° C.
1	1·14	1·0	1·13	1·0	1·12	0·9
2	2·3	1·8	2·25	1·8	2·2	1·8
3	3·4	2·7	3·4	2·6	3·4	2·7
5	5·7	4·5	5·6	4·4	5·6	4·4
8	9·0	7·3	8·9	7·2	8·9	7·0
10	11·2	9·1	11·1	9·0	11·1	8·6
12	13·4	10·9	13·3	10·8	13·3	10·4
14	15·6	12·8	15·5	12·7	15·5	12·1
15	16·7	13·7	16·6	13·6	16·5	13·0
16	17·8	14·6	17·7	14·4	17·6	13·9
18	20·0	16·7	19·9	16·2	19·8	15·7
20	22·2	18·8	22·0	18·2	21·9	17·4
22	24·3	20·8	24·2	20·2	24·1	19·0
25	27·5	23·8	27·3	22·8	27·2	21·8
30	32·8	29·0	32·6	28·0	32·5	26·6

TABLE XIX. (*cont.*).

Aromatic fractions with corresponding aromatic-free cuts.

% Aromatics by vol. for all columns.	Fraction 215—230° C.		Fraction 230—250° C.		Fraction 250—270° C.	
	% Arom. by weight.	An. pt. depression. ° C.	% Arom. by weight.	An. pt. depression. ° C.	% Arom. by weight.	An. pt. depression. ° C.
1	1·14	0·9	1·15	0·9	1·16	0·9
2	2·3	1·7	2·3	1·6	2·3	1·8
3	3·4	2·5	3·5	2·5	3·5	2·5
5	5·7	4·1	5·7	4·2	5·8	4·2
8	9·0	6·7	9·1	6·6	9·2	6·8
10	11·3	8·3	11·4	8·2	11·5	8·6
12	13·5	10·2	13·6	10·2	13·7	10·4
14	15·7	11·9	15·8	11·9	15·9	12·1
15	16·9	12·7	16·9	12·8	17·0	13·0
16	17·9	13·6	18·0	13·7	18·1	14·0
18	20·0	15·5	20·2	15·5	20·3	15·7
20	22·2	17·3	22·4	17·3	22·5	17·5
22	24·4	19·0	24·6	19·2	24·7	19·2
25	27·6	21·7	27·8	21·8	27·9	22·4
30	32·9	26·3	33·1	26·4	33·3	27·1

TABLE XX.

Average standard curve.

Addition of slumped aromatics to complete kerosene (see Fig. 5).

% Aromatics. By vol.	% Aromatics. By weight.	An. pt. depression. ° C.	% Aromatics. By vol.	% Aromatics. By weight.	An. pt. depression. ° C.
1	1·15	0·8	20	22·1	18·2
2	2·3	1·6	22	24·3	20·2
3	3·4	2·5	24	26·4	22·1
4	4·5	3·4	26	28·5	24·0
5	5·6	4·2	28	30·6	25·9
6	6·8	5·2	30	32·7	27·8
7	7·9	6·1	32	34·7	29·7
8	9·0	7·0	34	36·9	31·7
10	11·2	8·8	36	39·0	33·7
12	13·4	10·6	38	41·0	35·7
14	15·6	12·5	40	43·1	38·0
16	17·8	14·3	42	45·1	40·3
18	20·0	16·2	44	47·1	42·6

TABLE XXI.

Aniline-extracted aromatics from Burmah, American and Badarpur sources with aromatic-free kerosenes from the same sources.

The aromatic solutions as extracted had the following properties:—

	Burmah aromatics.	American aromatics.	Badarpur aromatics.
Sp. gr. 60° F.	0·892	0·876	0·932
Loss in conc. H_2SO_4	64%	53%	70%
An. pt. on dilution with 4 vols. arom.-free. kero. from same source ..	65° C.	66·8° C.	48·6° C.
An. pt. of diluted solution after 98% acid	76° C.	76·1° C.	60·2° C.
Conc. by volume of aromatics calculated on assumption that Table XX. is correct for all cases ..	12·4%	10·5%	13·0%
Conc. in original solution	62%	52·5%	65%

The concentrations were assumed to be 64 per cent., 53 per cent., 70 per cent. respectively, and concentrations by volume in the following cases are calculated on that assumption.

Aromatics. % by vol.	Burmah aromatic-free fraction. An. pt. 72·8° C. Depression.	American aromatic-free fraction. An. pt. 72·0° C. Depression.	Badarpur aromatic-free fraction. An. pt. 59·6° C. Depression.
(a) Burmah aromatics added to—			
5 ..	4·4 ..	4·6 ..	4·1
10 ..	9·0 ..	9·2 ..	8·1
15 ..	13·7 ..	13·6 ..	12·2
(b) American aromatics added—			
5 ..	4·5 ..	4·7 ..	—
10 ..	8·8 ..	9·4 ..	—
15 ..	13·4 ..	13·9 ..	12·0
(c) Badarpur aromatics added—			
5 ..	4·3 ..	4·5 ..	4·1
10 ..	8·7 ..	9·1 ..	8·0
15 ..	13·2 ..	13·5 ..	12·1

From the above tables it is seen that:—

(1) Depressions for a given percentage volume or weight of aromatics present vary somewhat for different aromatic fractions, giving minimum values for naphthalene and its lower homologues, but the discrepancies are not serious when slumped and the effects can be quite eliminated by taking cuts separately in the analysis.

(2) A correction should be applied when the naphthene content is abnormal (see comments on Table IX.).

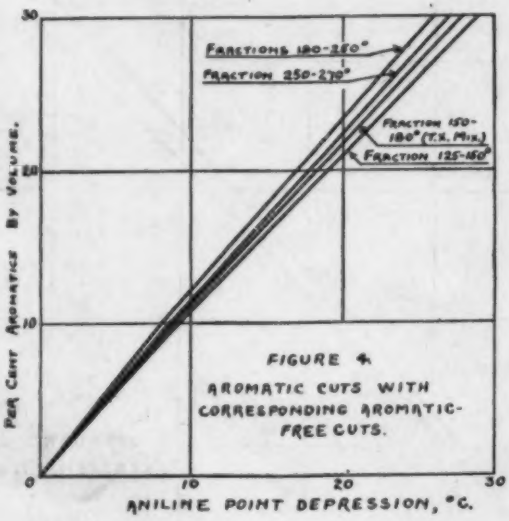


FIGURE 4.
AROMATIC CUTS WITH CORRESPONDING AROMATIC-FREE CUTS.

(3) The depression curve is not quite linear at very high concentrations, hence it is advisable to dilute a fraction of high aromatic content with a known quantity of the same aromatic-freed fraction if possible, in order to keep the depression of the aniline point, as shown by differences before and after acid treatment, to 20° C. or less.

(4) Figs. 4 and 5 give the results graphically and the graphs can be used as standards for calculation with sufficient accuracy for any purposes for which the test is applicable in practice. It is not of the accuracy of gravimetric analysis,

but there are very few cases in which greater accuracy is required, particularly if due attention is paid to corrections as mentioned in (2) above.

The table below represents an analysis of aromatics in an untreated kerosene fraction, obtained in three different ways:—

(1) By fractionating to the limits shown in the first column and calculating the aromatic contents from the results in

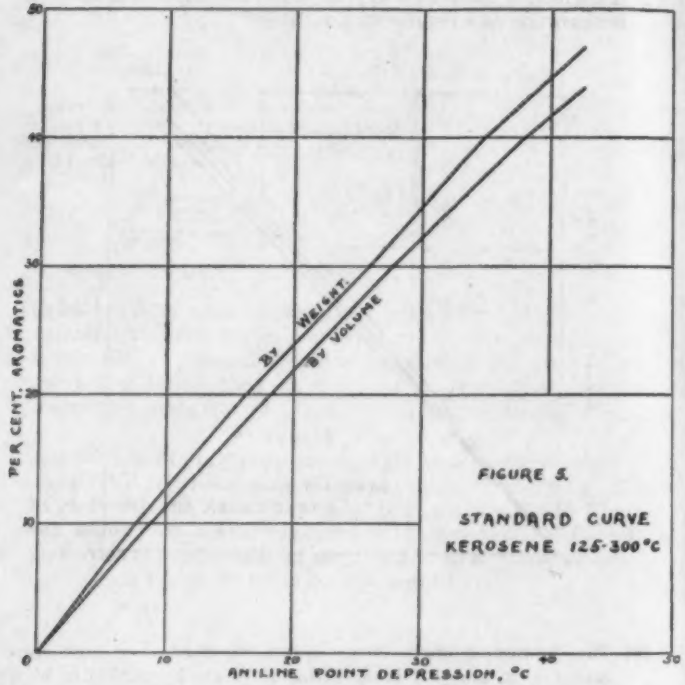


Table XIX. giving values for corresponding aromatics with aromatic-free cuts, Fig. 4.

(2) By cutting the same kerosene into two fractions, 125-215° C. and 215-270° C., using mean values calculated from the first and last three columns in the same table respectively.

(3) By treating the kerosene as a whole and applying the standard Table XX., Fig. 5.

TABLE XXII.

(1) By cuts.

Fraction.	% Cut on total.	% Aromatics by volume on cut.	% Aromatics by volume on total kerosene.
125—150 ..	19·1 ..	18·7 ..	3·6
150—180 ..	30·3 ..	20·7 ..	6·3
180—215 ..	21·3 ..	19·8 ..	4·2
215—230 ..	9·6 ..	18·7 ..	1·8
230—250 ..	12·4 ..	20·5 ..	2·6
250—270 ..	7·3 ..	23·9 ..	1·7
		Total ..	20·2

(2) In two cuts.

Fraction.	% Cut on total.	% Arom. on cut by vol.	% Arom. on total by vol.
125—215	70·7	20·3 (An. pt. 18·4° C.)	14·35
215—270	29·3	21·0 (An. pt. 18·2° C.)	6·15
		Total ..	20·5

(3) Complete.

Fraction.	% Arom. by vol.
Complete 125—270	20·3 (An. pt. 18·5° C.)
Total ..	20·3

In conclusion, it is mentioned that if papers have been published on similar themes after those appearing in the February number of this journal, any absence of acknowledgment by the writer here is due to non-receipt, as this paper has been written in Burmah and considerable delay between writing and publication is unavoidable.

The writer acknowledges the able assistance of Maung Maung, A.R.C.S., in part of the experimental work, also of Mr. N. G. Raye, M.Sc., and Mg Hla Oung, and wishes to thank the Directors of the Burmah Oil Company for kind permission to publish the work, also Mr. W. J. Wilson, F.I.C., for kind assistance in correcting proofs.

Torbanite and its Treatment by the Bergius Method.

By Professor A. W. Nash, M.Sc., F.C.S., M.I.Mech.E.

Introduction.

The origin of torbanite or boghead coal, and its genetic relation to other bituminous rocks or carbonaceous deposits, has been the subject of enquiry since about the year 1852, following on the famous lawsuit of Gillespie *v.* Russel to determine whether this material should be classified as coal or otherwise.

The present investigation was carried out as the result of a suggestion made by several members of this Institution, following a discussion on a previous paper by the author; torbanite from New South Wales was chosen in the hopes that it would bring once more before the public the possible future importance to Australia of the tremendous deposits of this material to be found in that State.

In his presidential address to the Royal Society of New South Wales, 1924, R. H. Cambage[1] stated that the total quantity of "Kerosene shale" (Australian term for torbanite) expected to be won from deposits in the State was approximately 40,000,000 tons, which would yield about 3,500,000,000 gallons of crude oil. Figures[2] obtained from those working in the Wolgan Valley mines show that the thickness of the torbanite in this area varies between 14 and 50 inches, and the yield of crude oil per ton of shale in actual practice averaged 100 gallons. The distillation products from the crude oil were found to be, under working conditions, as follows:—benzine, 5 per cent.; kerosene, 20 per cent.; gas oil, 25 per cent.; fuel oil, 20 per cent.; paraffin wax, 5 per cent.; loss in treatment, 25 per cent.; sulphate of ammonia, about 22 lbs. per ton of torbanite.

Mention of torbanite existing in New South Wales was made as far back as 1807 as the result of a French scientific expedition to Australia in 1802, but the value of this material was not brought to the notice of the public until 1850, when it was discovered at Torbane Hill; other deposits were subsequently discovered in Linlithgowshire, but this material is now worked out. It is on record, however,[3] that torbanite is still to be found in many countries,

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[1] Wade, "Report on Investigations made in New South Wales, 1925."
[2] Wade, *loc. cit.*
[3] Greene, "Treatise on British Mineral Oil," p. 41. Thiessen, "Origin of the Boghead Coals," *U.S. Geol. Surv. Paper* 132, p. 133, 1925.

particularly France, South Africa, many parts of England and Scotland, Nova Scotia, Pennsylvania, Kentucky and Alaska.

Besides kerosene shale, torbanite and torbanehill material, other names have been applied to these deposits such as brown cannel coal, bathvillite, algal coal, albertite, bituminite, parrot coal and cannel coal.

Torbanite, although considered to be a different material to oil shale, and often referred to as boghead coal, behaves, on distillation, exactly as a Kerogen shale : its carbon-hydrogen ratio is much lower than coal and the retort residue is not a coke or semi-coke such as coal would give, but an ash containing a very small proportion of carbon. In outward appearance it differs little from other bituminous shales and is often difficult to distinguish with the naked eye ; it is dark brown or dull blackish material having a dull yellow streak and breaks with a conchoidal or semi-conchoidal fracture : when ground to pass a fine mesh its colour is dark brown. Although stratified in the mass, it does not exhibit a laminated structure in the raw state similar to a true oil shale, neither will it split along definite planes ; but after retorting it shows similar properties to a spent shale.

Miscroscopic inspection is a good test for torbanite in that when thin sections are examined in this manner they are found to contain, or are largely composed of, irregular oval yellow bodies which renders this material easily distinguishable from ordinary Kerogen shales. These rounded yellow particles, about $\frac{1}{100}$th or $\frac{1}{200}$th of an inch in diameter, or even smaller, have caused considerable discussion among scientists as the composition of these granules is unknown.

The Scottish torbanite is stated by Steuart[4] to have been a mass of carbonaceous matter without structure mingled with stems or roots of trees showing structure, and the fossils were found throughout the bed and not merely on the surfaces of seams, as is general with coal ; the miscroscope showed the scalariform tissue of tree ferns and there were no fish remains. This material took fire readily, split, but did not fuse, burned with an empyreumatic odour, giving much smoke and left a considerable amount of white ash : it contained from 20 to 30 per cent. of clayey matter, mixed with carbon compounds of complex constitution which were not of the nature of petroleum, resin or true bitumen as proved by solvent action.

The composition of New South Wales torbanite, as given from an analysis of the richest Joadja Creek material by W. A. Dixon[4]

[4] Steuart, "Oilshales of the Lothians," p. 160. Petrie, *J.S.C.I.*, 1905, 24, p. 997.

is as follows:—C, 75·32; H, 12·05; O, 5·49; N, 0·28; S, 0·31; ash, 6·55 per cent. Pyrites is found in the torbanite and is probably the source of the sulphur. The ash has the following composition:—SiO_2, 77·12; Al_2O_3, 20·14; Fe_2O_3, 0·76; CaO, 0·30; MgO, ·45; P_2O_5, 0·65 per cent.

The ratio of volatile to fixed carbon in the richest torbanite of New South Wales is 16 to 1; the ash being 6 per cent. and average specific gravity 1·2, although a specific gravity as low as 1·008 has been recorded.

The question as to whether torbanite is a coal or not has been dealt with by a number of investigators in more or less detail.

Quecket[5] considered torbanehill material, on the grounds that any plants found in it were accidental and on account of its having a basis of clay, as not being a coal, although possessing some of the properties of coal. Balfour[5] expressed the opinion that torbanite was of the same class as black cannel coal and Redfern,[5] after investigation of the yellow bodies and on account of their presence in cannel coals, shared the same view and supported their plant origin.

Bennett[5] found no trace of vegetable structure but explained its bituminous content as a derivative of resinoid matter formed in the partly woody structure of coal which had escaped into the surrounding earthy substance and points to the fact, in confirmation, that it is always found in the neighbourhood of coal.

Clarke[5] considered torbanite to be an embryonic coal formed from local deposits of resinous wood, which would in time pass into ordinary coal, whilst Dixon[5] was of the opinion that it was probably derived from wax-producing plants in view of the yield of solid paraffins obtained.

In discussing the relation of petroleum to coal and to oil shale and their common origin from vegetable matter, Craig[5] states that between peat and anthracite there is every gradation of deposit of vegetable origin and claims it has been proved that the purest deposits, *i.e.*, those freest from inorganic contents, attain the coal stage earliest. Those deposits which contain much inorganic matter in a finely divided state, and consequently where carbonisation has been retarded, yield most oil on distillation, *e.g.*, the torbanites.

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[5] Quecket, *Micr. Soc. London Trans.*, 1853, **2**, pp. 34–36. Balfour, *Roy. Soc. Edin. Trans.*, 1854, **21**, pp. 187–193. Redfern, *Micr. Soc. Quart. Journ.*, 1855, pp. 106-127. Bennett, *Roy. Soc. Edin. Trans.*, 1857, **21**, pp. 173–185. Clarke, "Industrial Progress of N.S.W.," 1871, p. 449. Dixon, *Australian Assoc. Adv. Sci. Proc.*, 1887, **1**, p. 134. Craig, *Journ. Inst. Petr. Techn.*, 1916, **2**, pp. 238–273; 1923, **9**, pp. 344–367.

Origin of Torbanite.

The origin of torbanite has also been discussed by a number of investigators : *e.g.*, David[6] pronounced the view, after exhaustive researches on the Australian variety, of fresh water algal origin.

Reinhardt Thiessen[6] in a recent publication setting forth his conclusions as to the origin and classification of torbanite as a result of extensive and very complete investigations of the boghead coals, classifies the bituminous rocks of sedimentary origin into two categories—coals and bituminous shales, adding as a rider that no definite line can be drawn strictly between these two groups because of the fact that coal deposits may pass into bituminous shales. Coal, the mineral content of which is relatively low, is composed mainly of the residues of the ligno-cellulosic components of plant life, whereas the chief components of organic shale are ligno-cellulosic together with other matter as a result of degradation of carbohydrates such as resinous and spore matter, cuticular and other ceric matter, and oil-algal matter. It is on the origin of these predominant constituents he classifies bituminous shales into several well-defined groups, as follow :—

(1) Humic, if predominant organic matter is derived from the degradation of carbohydrates ; (2) spore, if derived from spores ; (3) ceric or waxy, if derived from waxy substances of plants ; (4) resinous, if derived from natural resins of plants ; (5) algal, if the predominant organic matter is derived from oleaceous algal. To the last he attributes the origin of torbanite as will be shown later.

The composition of torbanite, as revealed by its microscopic structure, has given rise to an immense amount of research with a view to explaining its origin, notably by the French scientists Bertrand and Renault[6] and later by Potonie of Berlin. The results of their investigations point to the organic matter being in the main composed of microscopic gelatinous algæ of different species together with innumerable bacteria, which are presumed to have lived in the ancient lakes, pools and swamps, and to have acted, the one upon the other, to produce the jelly like mass : in this jelly were also to be found, in suspension, spores, pollen-grains, plant cells, cuticles and other minute vegetable remains, which are stated to be non-essential to its formation.

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[6] David, *Linnean Soc. N.S.W. Proc.*, 1889, **4**, pp. 483–500. Thiessen, *loc. cit.*, 121, pp. 131–133. Renault, *Soc. ind. min. St. Etienne Bull.*, 1899, **13**, pp. 895–1191. Zalessky, *Com. geol. Bull. Petrograd*, 1914, **33**, pp. 495–507. Conacher, *Geol. Surv. Glasgow Trans.*, 1917, **16**, pt. 2, pp. 164–192. Macfarlane, "Fishes the Source of Petroleum," 1923, pp. 111–113. Craig, *loc. cit.* Jeffrey, *Proc. Amer. Acad.*, 1910, **46**, p. 273.

In discussing the nature and origin of boghead coal, Zalessky[4] mentions a phenomenon existing to-day, which is of interest in view of Thiessen's theory developed subsequently. In the Ala Kul lake of Turkestan is to be found an alga bearing a considerable amount of oil, which rises to the surface and accumulates on the shores, where it changes after contact with air from a dark green to a yellow-brown, elastic, rubber-like mass, which can be cut with a knife. On examination it was found that the structure of the algæ still to be seen in this rubber-like mass, resembled similar bodies in siliceous boghead material he examined. The nature of the rubber-like mass was not investigated.

Conacher,[5] in his examinations of oil shales and torbanites, stated that they are derived from the same substance as coal but that in their formation the resinous matter has played a more important part.

Macfarlane[6] considers torbanite and like deposits to be rich varieties of oil shale, or cannel coal, and traces the bituminous content to decomposed fish-constituents, and not to the decomposition of plants of resinous nature, spores, or algæ, advanced by other scientists. Referring to the torbanite deposits of New South Wales, he considers these are formed as the result of the wide destruction of great masses of fresh water fish life, which on decomposition has set free the oily product which has gathered round or between clay particles, minute fragments of leaves, spores and other debris. This has floated to a distance from the mass of decaying scales, teeth and bones, eventually settled with the clay particles as a fine argillo-bituminous precipitate, and subsequently become condensed and solidified under combined pressure, heat, and chemical transformation.

Craig[6] does not agree with Bertrand, Renault and Jeffrey, who claim the gels as vegetable fossils, but considers they were not solid bodies when the deposits were formed: he describes torbanite as merely a cannel containing sufficient colloidal inorganic matter, which has been subjected to the necessary pressure under adequate sealing; in other words, in a natural autoclave. In such conditions the oil begins to form in minute globules, which combine at once to form gels with the colloidal inorganic matter. From the evidence of the coaly matrix in which the gels are set, and also from the fact that coal seams are invariably associated, or in contact, with torbanite seams, he considers the process of carbonisation had already begun and the formation of oil globules was consequently restricted: otherwise the original material might have been converted entirely into petroleum.

The oval yellow bodies were not considered by Jeffrey[6] to be colloidal gelatinous algæ but to have been formed from the spores

of vascular cryptogams, these latter having been laid down on the bottoms of the shallow lakes of the coal period, the resulting bituminous rocks forming the mother substance of petroleum, the free product being a natural distillate of these materials.

The nature and structure of the yellow bodies composing the boghead coals has been exhaustively studied by Thiessen[6] by subjecting the Kerosene shales from Newnes, New South Wales; bogheads from Torbane Hill and Bathgate; and American torbanites from Alaska and Kiskiminetas Junction, Pa., to microscopic examination and by studying the growth and behaviour of the organisms which he claims are responsible for their formation: these are to be found at the present day living in the salt lakes and lagoons of South Australia resembling in some respects some of the blue-green algæ to be found, although the nature and chemistry of the cell wall show them to be of different species: Thiessen has suggested the name of "Elaeophyton," meaning oil plant, should be given this organism.

This sub-aquatic plant can be found near the Coorong, floating as a green scum on the surface of the water and which is blown to the south eastern shores by the prevailing winds: the living part of the cells is stated to be of an oval shape and relatively small, not over 0·0002 inches in length and 0·00012 inches in diam., and a considerable number of the organisms unite and form one body. The plant quickly solidifies, as a result of the hot weather, into sheets of a rubber-like material known as Coorongite.

De Hautpick[7] in describing Coorongite states that it is found at the high-tide mark of occasionally submerged sandy plains spread over a great area and is undoubtedly the dessicated remains of some substance, which had previously floated on the water, and which absorbs and unites with any matter with which it comes in contact, during the process of drying.

When heated Coorongite melts into a syrupy fluid, which retains its viscidity even after cooling.

Its chemical and physical properties are as follow:—[8]

	%
Moisture and volatile substances at 120° C.	0·8
Gaseous distillates with acid reaction	14·0
Oily distillate	69·2
Tarry matter and coke	10·1
Mineral matter	5·9

[7] De Hautpick, "Australian Min. Standard," 1923, pp. 1000–1001.
[8] Thiessen, *loc. cit.*, p. 129.

The oily distillate gave on redistillation :—

Fraction at 110° to 170° C.	6·7
170—240° C.	27·7
240—295° C.	25·3
295—300° C.	27·3
Residue	14·0

Ultimate analysis, ash free, dry basis :—

	%
Hydrogen	12·0
Carbon	79·7
Nitrogen	0·7
Oxygen	7·5
Sulphur	0·1

Coorongite is partly soluble in carbon bisulphide, chloroform, ether and benzol, the viscous soluble oil being of a yellow colour, which darkens on standing. Cumming[9] found that the soluble matter was unsaponifiable; its composition was C, 77·92; H, 11·69; O, 10·39 and molecular weight corresponded to the formula $(C_{10}H_{14}O)_8$, and he concluded it was of the nature of a mineral oil.

In his conclusions, Thiessen states that the study of "Elaephyton" furnishes distinct proof of the theory of the algal origin of the boghead coals. The plan of organisation, the structure, and even the form and size of the organism agree so closely with the corresponding character of the yellow bodies that constitute the boghead coals, as to leave no room for doubt of their close biological relation and their similarity in composition. The chemical nature of these organisms is so resistant to the agencies of putrefaction as to enable them, in a favourable environment, to survive the coal-forming process with more or less complete preservation in the forms found in the boghead coals. No theory of chemical changes from cellulosic or mucous substances into an oil or fat is necessary: the oil is such in the living plant.

The Coorongite represents the peat stage of torbanite.

Torbanite Oil.

Petrie[10] has made a valuable and comprehensive contribution to the knowledge of New South Wales torbanite, particularly in regard to the physical and chemical properties of the distillate obtained.

Preliminary experiments were carried out with solvents in order to discover whether any natural oil was present. Finely powdered

[9] Cumming, *Chem. News*, 1903, **87**, pp. 306–308.
[10] Petrie, *loc. cit.*, pp. 996–1002.

torbanite was agitated with pure dry ether, the extract separated and the residue washed till a colourless filtrate passed through, when the solution was distilled. The natural oil had the consistency of vaseline; its colour was reddish-brown with a dark green fluorescence by reflected light. When heated gradually it began to volatilise at 160° C., and immediately blackened. On cooling it set to a tough, rubber-like odourless solid with a dark brown colour. A similar experiment, for comparative purposes, was carried out on vaseline at a temperature of 260° C, and on cooling the residue very much resembled, in appearance, the residue from the oil.

The natural oil solidified at 30° C.; its boiling point was about 160° C.; $d_4^{20} = 0{\cdot}9516$; concentrated sulphuric acid produced no blackening but after some time a faint dark brown colour was produced. On treatment with bromine, substitution derivatives were formed (100 grms. of oil taking up 7 grms. of bromine) but no additive compounds.

The oil gave on analysis:—C, 85·27; H, 11·62; undetermined, 3·11 per cent., probably sulphur, nitrogen and oxygen.

The natural oil in the torbanite consisted, therefore, of saturated hydrocarbons of high boiling point, together with a small quantity of other compounds.

The crude oil, obtained by destructive distillation of the torbanite, which was of a greenish-black colour, and solid except in hot weather, showed, in thin layers, a dark brown colour with a dirty greenish tint by reflected light: much suspended matter was present, part of which settled to the bottom on long standing in a warm place, the sediment consisting of black solid particles, covered with a red film.

The density of the crude was 0·9035 ($\frac{20}{4}$). On heating gradually up to 150° C. over a number of days in an open vessel, 57·65 per cent. was volatilized, the residue forming a hard, but not brittle, pitch, which could not be drawn into threads and possessed no asphaltic nature; it was partly soluble in carbon bisulphide: 100 grms. of the crude oil absorbed 42·6 grms. of bromine, 12 grms. of bromine addition compounds and 15·3 of substitution compounds. When treated with 1 per cent. of sulphuric acid at 50° C. it lost 14 per cent. by volume as a thick black tar: the colour of the oil was then pure dark green, and the S.G. was reduced to 0·8875. Analysis of the oil gave:—carbon, 86·93; hydrogen, 11·96; nitrogen, 0·58; sulphur, 0·373 per cent.: ash content was 0·042 per cent.

The crude oil was found to be a mixture chiefly of paraffins and olefines, the latter forming 70 per cent. of the lightest distillate

up to 30° C. boiling point, after which they gradually decreased until 280° C. was reached, when they disappeared; the rest of the oil distilling between 280° and 400° consisted almost entirely of paraffins. The naphtha, which formed 9 per cent. of the crude oil, consisted of approximately equal parts of paraffins and olefines, with boiling points from 30° to 200° C., and specific gravity from 0·660 to 0·800. The paraffins present amounted to from 30 to 50 per cent., and from pentane up to undecane.

The solar oil (which included the Kerosene fraction) had a boiling range from 200° to 270° C., specific gravity from 0·800 to 0·870. It contained 50 per cent. of paraffins in the lightest fraction, increasing to 80 per cent. at the end boiling point: these were from dodecane to pentadecane. The heavy oil commenced to boil at about 270° C. when the cooled distillate began to show the crystallisation of solid paraffin; the specific gravity increased from 0·870 upwards. That fraction passing over between 270° and 300° contained the last trace of the olefines with penta- and hexa-decane. From 300° C. upwards the paraffins $C_{17}H_{36}$ to $C_{30}H_{62}$ made up the entire bulk of the heavy oil. This portion was solid at ordinary temperatures, and possessed a bright emerald-green fluorescence. At the end of the distillation, the last of the heavy oil was followed quite suddenly by the appearance of high-boiling solid hydrocarbons, of low-melting point, of the vaseline class.

In that portion of the oil boiling below 150°, benzene and its homologues were detected in minute quantities: a notable amount of phenols was also present, and a minute trace of thiophen.

By the action of sulphuric and nitric acid mixture on the various fractions after complete refining with concentrated sulphuric acid, naphthenes were also thought to be present, in some fractions in appreciable quantity.

Experimental.

The object of the following experiments was to determine whether torbanite would behave in a similar manner to coal when subjected to high pressure treatment as has been described elsewhere.[11]

The two samples of torbanite (I and II) were crushed to pass 60 mesh and subjected to treatment with hydrogen under pressure, up to temperatures of the order of 450° C. The apparatus used was the 2 and 3 litre autoclaves previously described (J.I.P.T. 1925, **10**, 904, and Fuel 1926, **5**, 139). Comparative experiments

[11] Shatwell and Graham, *Fuel*, Jan., Feb., March, 1925. Shatwell and Bowen, *Fuel*, June, 1925. Skinner and Graham, *Fuel*, Nov., 1925. Bowen and Nash, *Fuel*, Aug., 1926.

were also carried out in which an atmosphere of nitrogen replaced that of hydrogen. In the earlier experiments the material was heated for three hours, under pressure, with and without phenol as a liquid disperse medium. Great difference in the oil yields in the hydrogenation and nitrogen-blank experiments were observed, but in the former case although hydrogen absorption occurred, yet greater oil yields than those from destructive distillation did not result.

Analytical Characteristics.

	Sample I.	Sample II.
	%	%
Ash	24·22	12·38
Moisture	1·06	1·70
Volatile matter	55·30	72·23
Specific gravity	1·262	—
Sulphur content	0·59	—

Distillation.

The distillations were carried out in the assay apparatus of Gray & King, and also in the small aluminium retort of Fischer.

Sample	I.	II.	
Experiment	1.	1.	2.
Apparatus	Gray & King	Gray & King	Fischer
Weight used	20 g.	20 g.	50 g.
Max. temp.	440° C.	500° C.	450° C.
Water	0·4 g.	0·4 g.	1·0 g.
Oil	6·26 g. (31·3%)	11·15 g. (55·7%)	27·05 g. (54·1%)
Residue	12·40 g.	6·65 g.	18·52 g.
Gas (N.T.P.)	729	1100 c.c.	—

Steam Distillation.

Sample I was submitted to steam distillation in a modified form of the apparatus of Lomax and Remfrey, previously described (J. Inst.P.T., 1925, **10**, 878).

Sample I.

Expt.	1	2
Weight used	500 g.	500 g.
Oil	192·73 g. (38·54%)	175·68 g. (35·13%)
Gas	1·38 cu. ft.	1·25 cu. ft.

Characteristics of Oil:—Standard Distillation. I.B.P. 55° C.

Specific gravity	0·8900	Up to 100° C. 5%
Iodine value	831·5	„ 125 8%
		„ 150 11%
		„ 175 15%
		„ 200 19%
		„ 225 23%
		„ 250 29%
		„ 275 35%
		„ 300 42%

Hydrogenation of Torbanite.

Experiments I and II.

Sample I was treated with hydrogen under pressure in Experiment I, at an average temperature of 428° C. and in Experiment II at 443° C., in the 3 litre autoclave.

Table I gives details of the treatment:—

Table I.

	Experiment I.	Experiment II.
Initial pressure	58 atm.	67·5 atm.
Final pressure	45 „	53·0 „
Maximum pressure	135 „	145·0 „
Total loss in pressure	13 „	14·5 „
Duration of heating above 400° C.	3 hrs.	3 hrs.
Average temp. above 400° C.	428° C.	443° C.
Maximum temperature	452° C.	450° C.
Gas released	4·63 c. ft. at 16° C. and 754·3 mm.	5·3 c. ft. at 15° C. and 751 mm.
Gas analysis:—		
CO_2	1·0%	0·4%
CO	2·6%	1·4%
H_2	84·6%	89·7%
CH_4	11·7%	8·5%

The products from the autoclave consisted of mixtures of oil and solid matter. Separation was effected by filtration and subsequent extraction of the solid with ether. Experiment I yielded 78 g. of oil (39·0 per cent.) and 105·6 g. solid and Experiment II 61·5 g. of oil (30·7 per cent.) and 88·6 g. solid residue.

Examination of Products from Experiment I.

Oil:—$d^{15·5}$ . . . 0·9348; Iodine value (Wijs) 265·5; Analysis:—C=77·58 per cent., H=10·15 per cent.; N=0·73 per cent. S=0·24 per cent. Solid residue:—Ash=56·72 per cent.; moisture =0·49 per cent.; volatile matter=13·44 per cent.; fixed carbon =29·82 per cent.; sp. gr. 1·925. Analysis:—N=2·82 per cent.; S=3·25 per cent.

Experiment III.

A blank experiment was carried out in which 200 g. of Sample I was submitted to similar treatment as before, but in an atmosphere of nitrogen. It will be observed that an increase in pressure was noted as opposed to decreases in the hydrogen experiments. Table II gives the details of the treatment.

Table II.

	Experiment III.
Initial pressure	38·5 atm.
Final pressure	43·5 „
Maximum pressure	118·0 „
Total increase in pressure	5·0 „

TABLE II.—*continued.*

Duration of heating above 400°	3 hrs.
Maximum temperature	453° C.
Average temperature above 400°	449° C.
Gas released	5·05 cu. ft. at 14° C. and 749 mm.

Gas analyses :—

CO_2	2·0
CO	1·7
H_2	1·0
CH_4	24·3
Unsats.	4·8
N_2	66·2

The high proportion of methane suggests that decomposition of the oil had taken place under these conditions.

The product was separated into :—18·4 g. oil (9·2 per cent.) and 133·3 g. solid residue.

EXAMINATION OF PRODUCTS FROM EXPERIMENT III.

Oil :—$d^{15.5}$=0·9384 ; Iodine value 446 ; Analysis :—C=81·27 per cent. ; H=10·16 per cent. ; N=0·66 per cent. ; S=0·62 per cent. ; Solid residue :—Ash 40·90 per cent. ; moisture 0·57 per cent. ; volatile matter 12·40 per cent. ; fixed carbon 46·70 per cent. ; sp. gr.=1·697 ; nitrogen=1·67 per cent. ; sulphur=1·80 per cent.

EXPERIMENT IV.

The same amount of torbanite (sample I) as in the previous experiments was mixed with an equal weight of pure phenol, and treated with hydrogen at an initial pressure of 38·5 atm. Table IV shows the experimental conditions :—

TABLE IV.

Experiment IV.

Initial pressure	38·5 atm.
Final pressure	27·5 „
Maximum pressure	112·0 „
Total loss in pressure	11·0 „
Duration of heating above 400° C.	3 hrs.
Average temperature above 400° C.	442° C.
Maximum temperature	457° C.
Gas released	2·82 cu. ft. at 14° C. and 748·2 mm.

Gas analysis :—

	%
CO_2	2·2
CO	2·9
H_2	68·6
CH_4, etc.	26·3

This gas was also characterised by a high methane content.

The product was found to contain an oil insoluble in the phenol, a phenolic oil solution and solid residue. The phenolic solution was shaken with excess caustic soda and the oil liberated. The phenol soluble oil was extracted with ether and found to be partially soluble only. There was thus obtained :—(a) 40·02 g. oil soluble in ether and phenol ; (b) 10·8 g. oil insoluble in the phenol ; (c) 11·1 g. solid soluble in phenol but insoluble in ether ; and (d) 74·9 g. insoluble residue. The characteristics of these fractions are given in Table V.

TABLE V.

Examination of fractions from Experiment IV.

	Oil (*a*).	Oil (*b*).	Solid (*c*).	Solid (*d*).
Density	0·9671	0·7780	—	1·903
Iodine value	404	179	—	—
Ash	—	—	17·42%	55·09%
Moisture	—	—	5·45	0·75
Volatile matter	—	—	40·44	11·51
Fixed carbon	—	—	42·14	33·36
Ultimate analysis—	%	%	%	%
C	90·37	80·75	—	—
H	6·56	12·40	—	—
N	0·96	0·14	0·82	1·21
S	0·29	0·26	0·51	1·04

FURTHER EXPERIMENTS.

EXPERIMENTS V—VIII.

Two experiments were carried out with sample I involving three hours treatment at an average temperature of 450° in the 2 litre autoclave with initial pressures of 37·7 atm. (Experiment V nitrogen-blank and Experiment VI hydrogenation). Surprisingly small yields of oil were obtained, *namely*, 22·9 per cent. in Experiment VI and 10·2 per cent. in Experiment V as compared with the ordinary steam distillation yield of 38·5 per cent. oil. It was observed that the pressure on first reaching 450° was 122·4 atm. in the nitrogen experiment and 94·9 atm. in the case where hydrogen was used, both experiments commencing with the same initial pressure.

It was inferred from this that a considerable amount of the hydrogen absorption takes place during the initial thermal decomposition, Accordingly, two further experiments, VII and VIII, were conducted in which sample II was treated under the same pressure conditions as before but heating to 450° and allowing to cool so that the time above 400° was approximately 20 minutes.

In these experiments the risk of thermal decomposition of the oil was lessened, but again greater amounts of oil than from ordinary distillation were not obtained.

The products were removed from the autoclave and distilled to 400° in the aluminium retort. A further small amount of oil was recovered from the walls of the autoclave by washing with chloroform. Table VI shows the comparison of oil yields from destructive distillation, hydrogenation and nitrogen blank experiments.

TABLE VI.

Sample II.

Experiment.	Distillation.	Hydrogenation. Experiment VII.	Nitrogen-blank. Experiment VIII.
	%	%	%
Oil yield	54·1 ..	40·4 ..	32·8
Residue	37·0 ..	33·1 ..	39·9
Ash in residue	33·0 ..	30·5 ..	26·6

These oils were distilled up to 225° and distillate percentages are given in Table VII.

TABLE VII.

Fractions.	Distillation.	Hydrogenation. VII.	Nitrogen-blank. VIII.
	%	%	%
Up to 175° C.	11·6 ..	12·3 ..	13·9
175—225°	11·6 ..	14·8 ..	16·9
Above 225°	76·8 ..	72·9 ..	69·2

SUMMARY.

1. The application of the Bergius process to torbanite did not lead to greater oil yields in experiments with and without a liquid disperse medium (phenol).

2. The oils are liable to undergo thermal decomposition if the treatment is prolonged to any appreciable extent.

3. The results, although negative, afford information that under the experimental conditions stated New South Wales torbanite is not amenable to hydrogenation, as was found to be the case with the coals already experimented with under similar conditions in this department.

The author is indebted to Dr. A. R. Bowen for assistance in the preparation of this paper and for having supervised, and to Mr. W. Johnson for having carried out, part of the experimental work; for supplying samples of torbanite thanks are due to Mr. E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S. (Sample I) and to the Agent-General for New South Wales (Sample II).

Some Experiments on the Oxidation of Lubricating Oil.

By HAROLD MOORE, M.Sc. (Tech.), A.Inst.Mech.E., and JAMES BARRETT, A.M.C.T.

ALTHOUGH for some time past considerable attention has been paid to the oxidation of lubricating oils the writers are of the opinion that the importance of oxidation-resisting qualities in a lubricating oil is still under-estimated. Scientific research bearing on the practice of lubrication has been very largely confined to the property of oiliness, and in many quarters this is considered of primary importance. When dealing with commercial lubricants and their practical application, the authors are of the opinion that oiliness is of secondary importance, a much more important factor being resistance to oxidation. Apart from special conditions encountered in motor racing and in experimental machines of various types, one may say that the great bulk of machinery used at the present time is designed in such a way that the bearing surfaces are quite adequate and the temperatures encountered are not extremely high. As the factor of oiliness only comes into consideration when extreme bearing pressures are encountered and is of no advantage when a bearing is of sufficient dimensions and is adequately supplied with oil, one may say that in the majority of cases a great degree of oiliness is not called for in practical lubrication. Experience of failures in the lubrication of a large variety of machines has led the writers to believe that the majority of failures, where they have been due to the lubricant, are caused by oxidation of the oil, and would have in no way been saved by the use of a lubricant possessing a higher degree of oiliness. Naturally, a large proportion of the failures which are stated to be due to the lubricant are brought about by other causes, mainly mechanical ones, and in such cases it is extremely rare that a higher degree of oiliness would have been of any avail in preventing seizure or other contingent damage. The failures brought about by the lubricant can mainly be classed under two headings.

1. Because the lubricant did not possess sufficient oiliness to keep the bearings apart.

2. Brought about by inadequate supply of oil caused through the formation of deposits in the oil.

The former class of failure may occur where machines are of an experimental nature when the stresses are not fully understood by the designers, and therefore the bearing surfaces are inadequate.

Description.	Spec. grav. at 15° C.	Closed flash point, ° F.	Viscosity Redwood in secs.				Coke % Air Board specification.	Sludge test B.E.S.A. spec.	Acidity 100-g. oil neutralise mgr. KOH.	Oxidation test (Air Board spec.) after blowing for 12 hrs. at 200°C.				Sulphur content by bomb method. %	Viscosity Redwood in secs. Oil heated for 45 hours at 150 C without passing air through.				Proportional values before and after oxidation:		
										Viscosity Redwood		Coke test Air Board spec.	Acidity 100 g. oil neutralises KOH.						Coke %	Viscosity Redwood at 100° F.	Viscosity Redwood at 200° F.
			70 F.	100 F.	140 F.	200 F.				100 F.	200 F.				70 F.	100 F.	140 F.	200° F.	After/before	After/before	After/before
Russian pale oil ..	0·909	384	1180	387	132	56	0·19	0·72	6·0	880	70	1·09	140·0	0·17	1310	412	141	56	5·7	2·3	1·25
Californian red oil	0·928	354	1235	398	120	52	0·21	1·13	18·0	2660	158	4·69	212·0	1·32	—	—	—	—	22·3	6·7	3 0
Californian pale oil	0·928	355	1194	396	125	53	0·15	2·15	18·0	2370	128	4·28	220·0	0·66	—	—	—	—	28·5	6·1	2·4
South-American red oil	0·930	348	1130	354	123	52	0·87	1·78	12·0	very viscous	429	8·01	140·0	1·76	—	—	—	—	9·2	Probably over 20	8·25
Mixed base red oil (considered to be a mixture of Mid-continental and Pennsylvanian base)	0·910	425	1314	434	150	59	0·51	0·82	15·0	1010	95	3·50	140·0	0·58	—	—	—	—	6·9	2·3	1·6
Pennsylvanian long residuum ..	0·879	427	1595	612	211	74	0·55	0·35	9·0	900	112	2·94	140·0	0·10	—	—	—	—	5·4	1·5	1·5
Russian cylinder oil	0·912	417	2610	760	220	72	0·27	0·59	6·0	1210	88	1·55	110·0	0·15	2870	806	231	73	5·7	1·6	1·2
Texas red oil ..	0·939	355	1440	418	127	53	0·46	1·24	28·1	1320	99	2·68	234·5	0·58	—	—	—	—	5·8	3·2	1·9

High bearing pressures are also frequently encountered where shafts have run out of alignment, and in such cases a high degree of oiliness is useful and may prevent a breakdown. Where high bearing surfaces are brought about by wrong alignment it is probable that even if the lubricant possesses a high factor of oiliness it will still prove insufficient for the exceptional pressures encountered. In the majority of machines where the bearing surfaces are adequate, and the mechanical devices which supply the oil to the bearings function properly, it will be found that the majority of failures are brought about by a change taking place in the lubricant, altering its physical properties and thereby preventing the proper functioning of the pumps or other devices used to supply the oil to the bearing surfaces. In practice, the writers believe that the latter type of failure, due to inadequate supply brought about by change of the lubricant, is much more common than the failure caused by excessive bearing pressure. Where the actual mechanical devices employed for feeding the lubricant on to the bearing surfaces fail for mechanical reasons one may expect failure of the lubricant on the bearing surfaces irrespective of what its degree of oiliness may be, so that a high degree of oiliness in such a case would be of little use.

Failures brought about by change in the lubricant are almost entirely caused by the oxidation of the oil, which may either become of extremely high viscosity and refuse to flow through the circuit or may actually precipitate solid substances from solution. Further, the products of oxidation may become mixed with water and form jelly-like emulsions which will not pass through the necessary service pipes. The liability to form such emulsions with water is much greater when an oil has undergone a serious amount of oxidation. The possibility of appreciable oxidation taking place is not very great where oils are fed into a system in which they are slowly used and then completely lost, such as a drip-feed lubricator supplying a plain bearing, but the tendency in the design of modern machinery is strongly in the direction of providing lubrication in a continuous circuit from which oil is fed to the working parts, thence returned to a sump and again fed to the working parts by means of some mechanical appliance. Such systems are arranged to give a supply of lubricant considerably in excess of the requirements and providing the bearings are adequately designed there is little risk of failure unless the main oil supply should be insufficient or the oil should undergo such change as to interfere with its operation. Such continuous circuits are regularly encountered in the lubrication of turbines and practically every type of internal combustion engines. It is in such machinery that the necessity for an oxidation-resisting lubricant is most marked.

As the majority of lubricating oils used are made by the blending of various base oils with either thinner spindle oils or thicker filtered cylinder oils, it was decided that an investigation of the resistance of various oils to oxidation should be made with a view to noting the characteristics of oils of roughly similar viscosity originating from various sources. In view of this, the authors selected seven lubricants of fairly similar viscosity, and toward the end of the experiments a cylinder oil whose viscosity was considerably higher than that of the other seven was also tested as it was thought that the results would be of interest.

The oils chosen were as follows:—

Russian Pale Oil.
Californian Red Oil.
Californian Pale Oil.
Pennsylvanian Long Residuum.
South American Red Oil.
Mixed Base Oil (considered to be a mixture of Mid-Continental and Pennsylvanian base).
Texas Red Oil.
Russian Cylinder Oil.

The oils were first tested for ordinary physical readings. They were then subjected to the Michie sludging test, in which severe oxidation is encountered and the actual amount of hard asphalt is measured and stated in terms of weight of deposit per 100 grams of oil. The conditions employed are that the oil is heated for 45 hours at a temperature of 150° C. whilst air is slowly blown through the lubricant. On the completion of this period the hard asphaltum is precipitated with petroleum spirit and weighed. The resulting figure may be given as a measure of tendency to form deposits under very severe oxidising conditions. A further test with a view to demonstrating the tendency to oxidise was made by blowing air through the oil for 12 hours at 200° C., a test which is used by the Air Ministry in one of their lubricating oil specifications. At the end of this test the viscosity was redetermined and compared with the viscosity of the oil before oxidation. The coke value was determined by the Air Board method both before and after the oxidation test. As oxidation is accompanied by the formation of acids, it was deemed advisable to test the organic acidity of the oils before and after oxidation. When this test had been made it was decided to determine the sulphur content of the oils to see if the tendency to oxidation was in any way affected by the sulphur content of the oils.

The viscosities taken before and after blowing are given in terms of Redwood seconds, so that the increase of viscosity is

not correct if taken as the ratio between the two Redwood readings before and after, as for correct measurement these should be based on absolute readings. As, however, the differences are very great, it is not necessary to translate into terms of absolute, which would only make a comparatively small correction.

The results of these experiments are given in tabulated form below.

The South American Red Oil became so viscous under the 12-hour oxidation test that it was impracticable to determine the viscosity at 100° F., but it can be seen that this figure was very high from the high viscosity registered at 200° F.

The results indicate that Pennsylvanian Long Residuum and the Russian Pale Oil both show remarkable resistance to oxidation, giving both low sludge test and also showing little change in viscosity under oxidising conditions.

The asphalt base oils of higher gravity show considerable increase in viscosity, and the increases seem to be considerably affected by the sulphur content of the oils. The poorest results are obtained with the oils of highest sulphur content, and the best with the lowest sulphur content. For instance, the oil of highest sulphur content gives a coke value of over 8% after oxidation and increases in viscosity to a high degree.

The nature of the Pennsylvanian Long Residuum can be seen from the preliminary analysis, but since making these tests the authors have tested a Long Residuum with considerably lower sludge than this, from which one would imagine the Pennsylvanian Long Residua give exceptionally good tests in this respect. In fact, they recently tested one which gave a B.E.S.A. sludge test considerably under 0·1 per cent.

The oil which is listed as Mixed Base Red Oil is frequently referred as Pennsylvanian Oil, but in view of its high gravity the writers are of the opinion that it is probably a mixture of Mid-Continental and Pennsylvanian base.

The Russian Cylinder Oil was tested after the others, as it was thought in view of Russian Pale Oil having given such good tests it would be interesting to know what results one could expect from an oil of high viscosity but of the same base. The writers were curious as to the effect on heating without oxidation, and therefore put through a test on the two Russian oils, consisting of heating for 45 hours under conditions similar to the Michie sludge test but omitting the use of air. The figures are given in the tabulated results, and it will be observed that only a slight increase in viscosity has taken place. This increase is probably due to a trace of oxidation and perhaps to the removal of some of the lighter products by evaporation.

On the Accuracy of the A.S.T.M. Distillation Method.

(Communicated from the Laboratory of de Bataafsche Petroleum Maatschappij, Amsterdam.)

THE work herein described has been undertaken at the Amsterdam Laboratories of the Royal Dutch Shell Group in order to obtain an insight into the degree of accuracy, and reproducibility of the results, obtained by the A.S.T.M. method for the distillation of Benzines.

The "thermometer lag," *i.e.*, the rapidity with which various types of thermometers, *e.g.*, American A.S.T.M., German A.S.T.M., A.S.T.M. tube thermometers, etc., registered the same temperature was first investigated. No positive results could be obtained showing any constant difference between any two types of thermometer, the differences obtained being such that under similar conditions, one and then the other would register the higher temperature. In this connection mention may be made of the work of Dr. Ormandy[1] who using electrical measurement of temperature in the distillation of benzines, obtained differences of 15°-20° C. in the initial boiling points and 5-10° in the final boiling points compared with those registered by mercurial thermometers.

To examine the reproducibility of results, eighty distillations were carried out using a Sumatra benzine. Four different persons each performed five distillations on each of four different pieces of apparatus, all of which entirely met the specifications prescribed by the A.S.T.M. The thermometer readings were taken with an accuracy of ½° C. and the temperature of distillation was corrected to 760 mm. pressure in all cases, any correction of less than 0·25° C. being neglected. In each of the following tables, the average result obtained is taken as representing the truth, and the deviation from that average is described as the "error." Table No. 1 shows the results obtained in one series of distillations, by one of the observers (A.B.C. & D.) on one of the four sets of apparatus. (I., II., III., and IV.).

[1] *Journ. Inst. Petr. Techn.*, 1924, **10**, 43, 342-355.

TABLE 1.

Observer A.

Apparatus II.

	Temperature, ° C.					Average.
Initial boiling point ..	44	43·5	43·5	42·5	44	43·5±0·4
10 c.c. ..	70	70·5	70·5	70·5	70·5	70·4±0·15
20 ,, ..	78·5	78·5	78·5	78·5	78·5	78·5±0
30 ,, ..	85	85	84·5	85·5	85	85·0±0·2
40 ,, ..	90·5	91	91	91	90·5	90·8±·2
50 ,, ..	96·5	96·5	97	96·5	96·5	96·6±0·15
60 ,, ..	102	102	102	101·5	102·5	102 ±0·2
70 ,, ..	107	107	107·5	107·5	107·5	107·3±0·2
80 ,, ..	114	114	113·5	114·5	114	114 ±0·2
90 ,, ..	124	125	125·5	125·5	124·5	124·9±0·4
Final boiling point ..	151	147	151·5	150·5	150·5	150·1±1·2

From sixteen such tables incorporating the observations of A, B, C and D, on each apparatus I., II., III. and IV., Table 2 has been prepared.

TABLE 2.

Results of distillations carried out by four different observers.

	Observer A.		*Observer B.*	
	Average of 20 distillations.	Average error of observer.	Average of 20 distillations.	Average error of observer.
	° C.	° C.	° C.	° C.
Initial boiling point ..	46·45	±1·34	47·5	±1·24
10 c.c. ..	71·6	±0·65	72·3	±0·63
20 ,, ..	79·15	±0·36	79·5	±0·53
30 ,, ..	85·6	±0·37	85·7	±0·52
40 ,, ..	91·5	±0·40	91·5	±0·45
50 ,, ..	97·05	±0·34	97·0	±0·31
60 ,, ..	102·2	±0·27	102·4	±0·32
70 ,, ..	107·5	±0·30	107·9	±0·47
80 ,, ..	114·1	±0·30	114·3	±0·44
90 ,, ..	124·6	±0·44	124·9	±0·58
Final boiling point ..	149·4	±1·17	150·35	±1·20

	Observer C.		*Observer D*	
	° C.	° C.	° C.	° C.
Initial boiling point ..	47·4	±1·74	48·4	±0·80
10 c.c. ..	71·5	±0·86	72·8	±0·40
20 ,, ..	79·0	±0·86	79·6	±0·53
30 ,, ..	85·5	±0·77	85·95	±0·48
40 ,, ..	91·45	±0·71	91·85	±0·51
50 ,, ..	97·2	±0·78	97·25	±0·47
60 ,, ..	102·35	±0·87	102·35	±0·57
70 ,, ..	107·7	±0·44	107·9	±0·64
80 ,, ..	114·45	±0·39	114·2	±0·81
90 ,, ..	124·95	±0·99	124·85	±0·98
Final boiling point ..	150·9	±1·37	156·9	±2·00

This table records the average result of the twenty distillations performed by each man and each set of figures is independent of the variations produced by constant individual errors.

Table No. 3 records in a similar way the average of the figures obtained on each of the four pieces of apparatus used, and each set of figures similarly, excludes constant errors of the apparatus.

TABLE 3.

Results of distillations carried out with four different pieces of apparatus.

	Apparatus I.		Apparatus II.	
	Average of 20 distillations.	Average error.	Average of 20 distillations.	Average error.
Initial boiling point	° C. 48·3	° C. ±0·49	° C. 45·3	° C. ±1·09
10 c.c.	72·2	±0·37	71·2	±0·73
20 „	78·9	±0·36	78·65	±0·50
30 „	85·3	±0·37	83·1	±0·41
40 „	91·1	±0·26	91·05	±0·39
50 „	96·6	±0·20	96·7	±0·37
60 „	101·7	±0·35	102·1	±0·38
70 „	107·15	±0·33	107·6	±0·31
80 „	113·75	±0·52	114·05	±0·36
90 „	124·2	±0·65	124·7	±0·50
Final boiling point	151·6	±1·49	151·81	±2·70
	Apparatus III.		Apparatus IV.	
Initial boiling point	° C. 47·05	° C. ±0·81	° C. 49·2	° C. ±1·33
10 c.c.	71·9	±0·65	72·85	±0·65
20 „	79·4	±0·43	80·3	±0·56
30 „	85·8	±0·32	86·6	±0·49
40 „	91·6	±0·35	92·3	±0·46
50 „	97·2	±0·29	98·0	±0·49
60 „	102·25	±0·23	103·2	±0·60
70 „	107·8	±0·22	108·4	±0·58
80 „	114·4	±0·28	114·9	±0·56
90 „	124·55	±0·34	126·15	±0·97
Final boiling point	150·6	±2·27	153·6	±2·86

The average error in Table No. 3 will be seen to be slightly less than that of Table No. 2. It therefore follows that the error due to the apparatus is larger than that due to the individual; this is not true of the final boiling point figures. It may be seen from Table 2 that observer D has found the average final boiling point to be about 7° C. higher than those obtained by the three other observers. This was found to be due to the manner in which this observer interpreted the A.S.T.M. prescription for this determination. According to the A.S.T.M. prescription the flame may be increased after the 90 per cent. point has been reached, so that not more than five minutes elapse between the 90 per cent. and final boiling point. A. B and C interpreted this in such a

way that immediately after the 90 per cent. point the flame was moderately increased, D on the other hand, considerably increased the flame after 95 per cent. had distilled. Since D's interpretation does not contravene the A.S.T.M. prescription, the results have been included although in the following analysis of the results, the figures given, bracketed, exclude D's results.

TABLE 4.

Average result of 80 distillations.

	Average.	Average error of the result.	Average error of the separate observers.
	° C.	° C.	° C.
Initial boiling point	47·45	±0·15	±1·38
10 c.c.	72·04	±0·06	±0·74
20 ,,	79·31	±0·07	±0·62
30 ,,	85·68	±0·06	±0·56
40 ,,	91·56	±0·06	±0·53
50 ,,	97·12	±0·06	±0·50
60 ,,	102·32	±0·06	±0·55
70 ,,	107·74	±0·055	±0·49
80 ,,	114·27	±0·06	±0·52
90 ,,	124·83	±0·09	±0·78
Final boiling point	151·90	±0·28	±2·46
	(150·23)	(±0·17)	(±1·30)

From this table it will be seen that the error is largest at the initial and final boiling points and diminishes considerably in the middle of the distillation range. As might be anticipated (Table No. 1) this error is smallest when the distillations are carried out by one observer on one apparatus, as individual error and that due to the apparatus are then excluded from the results. Under these circumstances the average error for the initial and final boiling point is 1° C. or less and 0·2° C. in the middle of the distillation range, The error in these observations becomes 1·3° C. and 0·4-0·5° C. respectively when one observer is working with more than one apparatus (Table No. 2), and finally when both the errors due to the observers and apparatus are included the initial boiling point error is (Table No. 4) 1·4° C., middle of distillation more than 0·5° C. and final boiling point 2·5° C. or 1·30° C.

It should be noted that since the figures quoted as average error, may be positive or negative the total variation to be expected in an actual determination is at least equal to twice the figure recorded as average error. In the present instance the accuracy of the determination of initial and final boiling points excluding D, is 3° C. which is within the limit of 3·33° C. prescribed by the A.S.T.M.

A further fact which has been determined in the course of this work is the accuracy with which the volume of a benziné distilling to a certain temperature, can be determined, *e.g.*, the percentage

distilling to 100° C. This must be equal to the accuracy of the temperature reading, multiplied by the cotangent of the angle of the distillation curve at the selected point. In the present instance this value of the cotangent at 100° C.=2·0 approx. and from Table No. 4 the error of thermometer reading=$\pm$0·5° C. approx. at 100° C. consequently for the benzene under examination the error of the percentage passing over to 100° C. will be equal to $\pm$1 per cent. approx., *i.e.*, a total of 2 per cent. approx. This value is clearly largely dependent on the slope of the distillation curve and for a curve of steeper slope the cotangent will decrease and the percentage accuracy of the determination increase.

The Main Constituents and Possible Utilisation of Primary Tar.*

By Christopher John Ward.

There can be no doubt that the burning of raw coal is a wasteful method of use, since valuable by-products and an efficient smokeless fuel can be obtained by carbonisation at temperatures about 600° C.

The first patents for the production of a smokeless fuel date from 1906 when Parker produced "Coalite" by carbonisation of coal at 500° C.

Scientific investigation of the distillation of coal under varying conditions has put forward much valuable information. In 1906 Bornstein fractionated eight Westphalian coals in 50 degree stages up to 450° C., and showed the tars to contain paraffins and higher phenols, but not anthracene and naphthalene. In 1913 Pictet and Bouvier distilled a French bituminous coal in vacuo up to 430° C. They obtained a thin tar 4 per cent. by weight of the coal. This tar contained both saturated and unsaturated hydrocarbons, some oxygenated products but no phenols.

The saturated compounds were carefully examined, and certain definite hydrocarbons were identified such as hexahydromesitylene (C_9H_{18}) in the naphthenic group and dihydrotrimethylbenzene (C_9H_{14}) in the unsaturated group, together with several paraffins. A marked similarity was noted between these naphthenes and those of American petroleum.

In 1914 work was conducted on similar lines on British coals by Wheeler and others. The time of distillation was five weeks as compared with five hours by Pictet and Bouvier. The tar amounted to 6·5 per cent. by weight of the coal carbonised. A year later Jones and Wheeler distilled separately the cellulosic and resinic constituents of a coal and obtained two quite different tars. The cellulosic coal yielded very little tar composed chiefly of phenols, whereas the resinic portion yielded 40 per cent. of its weight of tar which consisted of paraffins, olefines and naphthenes, but no phenols. Temperatures up to 400° C. were employed for distillation.

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* Paper read before the Birmingham Branch of the Students' Section on May 11th, 1926.

Solvent extraction to obtain oil from coal does not seem to afford much promise. Among the solvents used are alcohol ether, chloroform, acetone, aniline, petroleum, benzene phenol, and pyridine. Fischer has extracted coal and other bituminous substances with anhydrous sulphur dioxide. A dark red limpid oil was obtained on removal of the solvent, and the former on steam distillation yielded an oil with an agreeable petroleum odour. A residue containing deep yellow substances boiling between 200-250° C. was formed, and this on standing for some years in contact with air showed no visible alteration.

Much valuable work has been put forward by Fischer and his collaborators. For the distillation of coal on a small scale a thick-walled aluminium retort, provided with a ground-in cover and outlet tube of special design, was used. The retort is fitted with a lateral bore for the insertion of a thermometer. The high thermal conductivity of the aluminium and the thickness of the walls ensures uniform heating of the coal. For the production of larger quantities of tar Fischer has designed a rotating cylindrical retort made of sheet metal. The drum is provided with a steam inlet at one end, and at the other with a dust separator and stuffing box, through which the gas and tar vapours pass to the condenser.

Fischer attributes the following properties to a true primary tar:—Fluidity at room temperature, possible slight separation of paraffin wax, specific gravity at 25° C., 0·95–1·06 golden red or port wine colour in thin films; when freshly made it should smell of hydrogen sulphide and never of naphthalene.

Primary tar from brown coal is richer in wax than that from bituminous coal and has a setting point of about 35° C., whilst the bituminous coal primary tar is poor in wax and rich in phenols.

Fischer investigated very thoroughly two coals:—Lohberg coal (meta lignitous) which gave 10 per cent. of its weight of tar, and Osterfeld coal (meta bituminous), a typical coking coal, which yielded 3 per cent. of its weight of tar. The tars from these coals were examined for light naphtha, lubricating oils, solid paraffins and phenols. The lubricating oil fraction was 15 per cent. of the Osterfeld primary tar and 10 per cent. of the Lohberg tar. The value of lubricating oils from low temperature tars is a debatable point, as they are deficient in certain qualities, *e.g.*, stability to air.

The large proportion of phenols in bituminous coal primary tar has led Fischer to investigate their possible utilisation. The conversion of phenols into motor fuels by elimination of oxygen to form homologues of benzene, by passage of the vapours with hydrogen through iron tubes at 750° C., gave very satisfactory results.

Separation of Primary Tar Without Temperature Changes.

The chief obstacle in the production of fuels from tar is the presence of pitch and the formation of further amounts of pitch on distillation. In 1870 Jacobsen showed that the asphaltic constituents of coal tar could be precipitated by the addition of petroleum ether.

A practical application of this principle was made by Lessing in a plant designed to wash tar with a non-aromatic hydrocarbon spirit thereby precipitating the pitch. The light spirit is redistilled and used over again in a continuous operation. The tar is first topped to remove benzol. The temperature of the mixing chamber is maintained at 60°–100° C. by steam heating.

In 1922 Brittain, Rowe and Sinnatt effected the resolution of two tars into their main constituents on these lines. The tars were treated with an equal volume of ether and a solid was precipitated which was separated by filtration. Carboxylic acids were obtained by washing the ethereal solution with sodium carbonate solution, and by acidifying the latter the acids were extracted with ether. The phenols were recovered from the ethereal solution by washing with caustic soda solution, acidifying and extracting with ether. The bases were recovered from the ethereal solution by extraction with dilute sulphuric acid, neutralising the washings, and finally extracting the bases with ether. The remainder of the ethereal solution was considered to be the neutral oil portion, and this was recovered after evaporation of the solvent.

The author has examined a low temperature tar in a similar manner. The tar examined was produced from a 7/30 blend of Arley and Butterley coals by carbonisation at a temperature of 620° C. in a vertical cast-iron retort.

The tar was a fresh sample and contained appreciable quantities of water. For the precipitation of the insoluble solid, an optimum quantity of ether was necessary. It was found that 200 c.c. of ether to 100 c.c. of tar could not be filtered owing to clogging of the pores of the filter paper. If 300 c.c. of ether were used with 50 c.c. of tar, the solid precipitated—Solid A—was precipitated slowly taking several days for complete separation. Finally it was decided that 400 c.c. of ether with 20 c.c. of tar completely precipitated Solid A in twenty-four hours, and filtration was quick and easy. The ethereal solution was then washed twice with 100 c.c. of 8 per cent. sodium carbonate solution. The alkaline solution was washed with 50 c.c. ether to remove traces of dissolved phenols, and the solution combined later with main phenolic solution. The sodium carbonate solution was acidified

with dilute sulphuric acid and extracted with two successive portions of 100 c.c. of ether. This ethereal solution, after drying over anhydrous sodium sulphate, was evaporated and the acids separated. There were only traces of the acids present. The ether solution remaining after the sodium carbonate treatment was washed twice with 100 c.c. of 10 per cent. caustic soda solution to remove the phenols. A small quantity of solid which was not estimated, separated between the two layers. The ethereal solution was washed with water to remove traces of caustic soda and the washings combined. The phenate solution was neutralised with dilute sulphuric acid, and the phenols extracted with ether.

This latter operation caused the precipitation of a black sticky solid which was obtained in the form of a brown powder after continued washing with ether. After removing the phenols by means of caustic soda solution, a further precipitation of Solid A occurred. The presence of the solid at this stage, Sinnatt accounted for by "solute" action, owing to its remarkable solubility in the phenol portion. Only a very small amount of solid was precipitated at this stage as an excess of ether was used for the original solution of the oil. Having separated the solid, the solution was washed twice with 100 c.c. of 14 per cent. sulphuric acid. The acid layer contained the bases and these were freed by neutralisation with sodium carbonate, and extracted with ether. The solution of bases was dried with sodium sulphate and the ether distilled off, leaving a brown liquid. When the bases were extracted with ether from the neutralised solution a very small quantity of a brown powder was precipitated. The ether solution remaining after washing with acid was dried with sodium sulphate and the solvent distilled off to give hydrocarbon and neutral oils.

The results of this separation are summarised in the following table:—

Solid A.	Initially precipitated by ether	2·77 g. per 100 g. of tar.
„	Precipitated after alkaline extraction of phenols	0·19 „ „ „ „
„ B.	Deposited from phenols	0·84 „ „ „ „
„ C.	.. ..	trace.
Phenols	.. ..	27·09 g. per 100 g. of tar.
Bases ..	.. ..	6·63 „ „ „ „
Carboxylic acids	.. ..	trace.
Neutral oil	.. ..	59·11 g. per 100 g. of tar.
Water and losses	.. ..	3·37 „ „ „ „
		100·0

Specific gravity of tar = 1·056.
„ „ neutral oil = 0·975.
Flash point of tar = 118° F.
„ „ neutral oil = 121° F.

The Working Up of an Old Tar.

Low temperature tars are known to change to some extent in character on standing.

A tar which had been allowed to stand for some months, and which had been originally obtained from a mixture of a coking and non-coking coal, was worked up in the same way, giving the following results :—

Solid A	7·55 g. per 100 g. of tar.
Solid B	5·11 „ „ „ „
Solid C	trace.
Phenols	25·29 g. per 100 g. of tar.
Bases	4·63 „ „ „ „
Acids	trace.
Neutral oil	53·65 g. per 100 g. of tar.
Water and losses	3·77 „ „ „ „
	100·00

Neutral Oil.

Standard Distillation.
I.B.P. 50° C.

Fraction to 75° C.	7 c.c.
75—100° C.	13 „
100—125°	14 „
125—150°	15 „
150—175°	16 „
175—200°	18 „
200—225°	28 „
225—250°	36 „
250—275°	48 „

Original Tar.

Standard Distillation.
I.B.P. 78° C.

Fraction to 100° C.	8 c.c.
„ 150°	10 „
„ 200°	16 „
„ 250°	41 „

After washing the ethereal solution with each reagent a trace of solid was noticed, and on standing for any length of time further small amounts of solid were deposited. The precipitation of solid from the solutions is therefore probably a time reaction.

The figures obtained are comparable with those obtained by Sinnatt, and the yield of phenols is appreciably lower than those quoted by Fischer.

The tar retained water with great tenacity.

Scheme for Separation of Low Temperature Tar.

Summary.

This paper is intended to show the lines on which former work has been carried out on the working up of primary tar, and also to give an account of the experimental separation of two tars into their main constituents.

After the separation of the tar, the problem arises for the utilisation of the products obtained.

This problem has been investigated by the German school to some extent, but still provides many fields for future research.

REVIEWS.

TREATISE ON SEDIMENTATION. William H. Twenhofel. Pp. xxv+661. London: Baillière, Tindall and Cox. 34s.

IN a "Treatise on Sedimentation" Mr. William H. Twenhofel, aided by an enthusiastic band of collaborators, has attempted to collect everything that is known about deposits of every kind, clastic, chemical and organic, formed on the surface of the earth. The evidence concerning each is critically examined, and the subject matter is chiefly descriptive, though theoretical points have to be dealt with here and there. Let it be said at once that the attempt is remarkably successful: the book is a mine of information and which should be in the possession of every geologist. It is worthy of study, not only by the beginner, but by the most advanced student of geology, and no field geologist ever gets beyond the position of student, however it may be with the academic geologist. It would be well indeed if everyone who has to undertake geological work in oilfields was familiar with this book. It would teach the field observer to give more attention to the modes and formation of all the different strata with which he has to deal, and thus might lead him to the solution of many difficult problems.

From the petroleum technologist's point of view, the most interesting part of the book is that dealing with carbonaceous sediments (pages 266 to 316), but there are many other passages that have a direct bearing upon oilfield problems.

The relations of coal, and carbonaceous deposits generally, to petroleum have necessarily been given prominence, while on the animal origin theory two passages are worth quoting. The author states on page 293: "The theory of the origin of petroleum from animal fats and oils is predicated on the preservation of the fatty animal matter or fatty acids of animal origin in the deposits through the peat stage and on beyond into the sphere of subsequent dynamochemical action. The study of the fossil sapropelic deposits has not yet lent tangible encouragement to this view. It would seem that only under conditions so exceptional as to be little short of cataclysmic so as to cause simultaneous and exceptionally abrupt killing of the animal population with coincident accumulation and deep burial of the dead matter can soft parts of the animals be preserved in accordance with the requirements of this theory."

Again on pages 308-9: "It is the belief of many that salinity is essential to oil generation. The arguments to this effect now pressed by Hoefer and others are largely based on insufficient tests in the laboratory, incomplete and inadequate field observations, and lack of knowledge of the paleontological and chemical composition of the organic debris composing the richest organic deposits.

"A briny medium, if sufficiently dense, would tend to conserve the animal fats, but in a brine of such strength the fish and other animals could not live, and it is certain that no such marked salinity prevailed when the fossil fish were alive. Nor can it be assumed that after the death of the fauna the salinity increased so rapidly or catastrophic entombment took place as to preserve the animal remains before microbian action was complete. The extraordinary, or even semi-cataclysmic, conditions under which animal tissues have been preserved are so restricted and rare as to be utterly inadequate as an explanation of the widespread occurrence of oil."

The claims of the obsolete, but in its time very useful, term Kerogen to denote a "special chemical substance" are rightly dismissed as having "no scientific foundation" (p. 309).

In dealing, however, with peats and torbanites, the obsolete, or obsolescent, term sapropel is still employed, and the author is hardly up to date in his treatment of "bogheads" or torbanites, referring to them on the old theory as "algal coals." This has been frequently disproved, and recently the latest published work of Professor A. E. Flynn of the Nova Scotia Technical College, Halifax, has finally disposed of the alga theory. This, however, is but a minor blemish in a treatise that deals very impartially and judiciously with the relation of carbonaceous and bituminous deposits of all kinds. It is in the collection and arrangement of facts from all parts of the world, particularly from the United States, that the great value of the work lies: when further research is necessary to decide any particular point, it is frankly stated, and an indication given as to the line of investigation to be followed. The book is copiously annotated with reference to authorities, showing what widespread work and reading has been necessary for the compilation of such a treatise and the condensation of the gleanings into a book of little more than six hundred pages.

The photographic illustrations are excellent, and the graphs and tables most suggestive and valuable.

Finally there is a chapter upon the study of sediments, both in the field and the laboratory, that is to be especially commended to field geologists as a help in learning all that is to be learnt about the strata they have to investigate.

E. H. C. C.

THE GEOLOGY OF OIL, OILSHALE AND COAL. Murray Stuart, D.Sc., Ph.D., F.G.S., F.C.S. Pp. viii + 104. London: Mining Publications, Ltd. 7s. 6d.

Dr. Murray Stuart has written a very interesting little book, which will give cause for thought, and probably comment, to many geologists. Much of the book is distinctly argumentative, but it is founded upon Dr. Murray Stuart's own observations in India and other countries, and if the propositions that he sets forth are occasionally somewhat startling, the arguments in their favour are at least closely reasoned, and in most cases quite a plausible case is made out. To give a few instances, he maintains that oilfields are the result of the deposition of petroleum along with argillaceous sediment, that coal seams are formed from carbonaceous matter that has been carbonised under fresh water conditions and has subsequently been carried out to sea and deposited under marine conditions, that lignites, on the other hand, have been formed under fresh or brackish water conditions as detrital beds, and that a lateral passage from coal seams through cannels and torbanites into oilshales or even true oil bearing beds is possible. All these propositions will, no doubt, be combated on questions of actual fact and observation. Other theories that he puts forward are that petroleum can be produced from lignites by dynamic action, *e.g.*, earth movement producing a thrust, and that limestone oils, or rather petroleum which is found in dolomitised limestone, have been formed from the organic remains of foraminifera attacked by sulphur forming bacteria at the bottom of inland seas or gulfs where the bottom waters are too poisonous to support other living organisms.

These latter propositions are chiefly theoretical, and the criticism that will occur to most readers is that Dr. Murray Stuart depends rather too much upon assumptions. When the author relies not upon his own obser-

vations, but upon statements by others, he is occasionally unfortunate, since some of the statements that he quotes are not in accordance with the facts.

The greater part of one chapter, dealing with Burma, has already appeared in an article published in the Journal, but the map and section through the Yenama field that he gives will certainly not be accepted as a true representation of structure by geologists who have an intimate knowledge of the Burma fields.

But all things considered, it is a challenging book that will compel geologists to review the facts concerning the formation of coal, lignite and petroleum, as known to them, and to apply those facts either to confirm or refute Dr. Murray Stuart's theories.

Possibly an exhaustive study of surface tension and of cannel coals and torbanites would solve many of the author's difficulties, and furnish him with simpler explanations for some of the phenomena he describes.

The book bears evidence of having been written hurriedly. There is a serious contradiction between passages on pages 57 and 67 on the subject of the relation of lignites to oil in Burma. E. H. C. C.

THE THEORY OF EMULSIONS AND EMULSIFICATION. W. Clayton, J. and A. Churchill. London: 7, Great Marlborough Street. 9s. 6d. net.

This book, of some 160 pages, published in 1923, gives an accurate summary of scientific knowledge respecting the behaviour and properties of emulsions. The subject matter is contained in nine chapters, the first of which is in the nature of an introduction to the subject, and deals with the general characteristics of emulsifying agents. The second, dealing with properties of emulsions covers rather too much ground for a single chapter, and might well have been expanded into two, together with more detailed mathematical explanations. The next twenty-one pages describe earlier theories of emulsions, and are invaluable to those who wish to gain a proper perspective of the purely theoretical side of the subject.

Adsorption at liquid—liquid interfaces is dealt with in chapter IV. and is certainly one of the most important sections of the book. A simple development of Gibbs' equation is given, connecting concentration of the solute at the interface with surface energy. Freundlich's "adsorption isotherm" receives a short explanation as does also Nugent's work on "Rates of Adsorption."

In addition, the chapter deals with "Angle of contact," "wetting of emulsifiers" and the "orientation theory."

Chapter V. constitutes a summary of the work of various investigators on "dual emulsions" and the "inversion of phases," and is followed by an account of the growth of the modern "adsorption film theory."

The seventh chapter deals with physical measurements in emulsions and comprises methods of determining interfacial tension using the drop-pipette, the determination of phases by (*a*) the indicator method, (*b*) the drop dilution method and (*c*) the electrical conductance method, and, finally, analysis of emulsions by nephelometry.

Chapters VIII. and IX. deal with some of the practical applications to industry and research, of the theories already described. The former chapter is devoted mainly to homogenisation, while the latter, dealing with de-emulsification should prove particularly useful to petroleum technologists whose work is connected with oil-field emulsions.

The book concludes with an excellent bibliography which contains references to practically every paper of importance dealing with emulsions.

W. H. T.

PETROLEUM DEVELOPMENT AND TECHNOLOGY IN 1925. 784 pp. New York: American Institute of Mining and Metallurgical Engineers, 1926.

This contains the papers presented at the meetings of the Petroleum Division of the American Institute of Mining and Metallurgical Engineers at Casper, Wyoming, Aug. 28–30, 1925, Los Angeles, California, Jan. 21, 1926, and New York, Feb. 15–17, 1926.

The book is divided into six parts, dealing with Introduction, Production Engineering, Refining Technology, Transportation Engineering, Production and Petroleum Economics. Each part contains papers, and discussions thereon, by authors whose names are well-known in the petroleum industry.

The whole work is an excellent treatise on the present state and trend of the Industry, and can be recommended as a valuable acquisition to all who desire to keep in touch with the up-to-date developments in the technology of petroleum. It is to be regretted that no index has been included. G. S.

BOOKS RECEIVED

POWER ALCOHOL PRODUCTION. *Ministry of Agriculture and Fisheries.* 14 pp. 1926. H.M. Stat. Office. 6d. net.

The report of the Departmental Committee appointed in connection with the production of Power Alcohol from Sugar Beet. Deals with cost of alcohol production, the comparative value of alcohol for power purposes, the production of alcohol by synthetic means, and also the production of liquid fuel from coal by low temperature carbonisation and by the Bergius process.

CARBONISATION OF COAL IN CONTINUOUS VERTICAL RETORTS. "HOLMSIDE" (DURHAM) COAL WITH EXPERIMENTS ON THE PRODUCTION OF COAL GAS OF HIGH CALORIFIC VALUE. *Fuel Research Technical Paper No.* 15. 45 pp. 1926. H.M. Stat. Office. 1s. 3d. net.